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Greenhouse gas emissions from Scottish arable agriculture and the potential for biochar to be used as an agricultural greenhouse gas mitigation option

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Doctor of Philosophy

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2014

Declaration

I confirm that the work submitted is my own, except where work which has formed part of jointly-authored publications has been included. The contribution of myself and the other authors to this work is explicitly indicated below. I confirm that appropriate credit has been given within the thesis where reference has been made to the work of others.

The work in Chapter 5 (Managing fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities) is based on work from a jointly authored manuscript of the same title which has been submitted to the journal *Geoderma Regional*. The work in Chapters 6, 7 and 8 is also based on work from jointly authored manuscripts which have not yet been submitted to journals. I am lead author on all of these manuscripts and as such undertook the vast majority of the work described in Chapters 5, 6, 7 and 8.

Nicola Winning

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Abstract

Nitrous oxide (N_2O) is a powerful greenhouse gas (GHG) which has a global warming potential 296 times greater than that of carbon dioxide (CO_2). Agriculture is a major source of N_2O and in the UK approximately 71 % of N_2O emissions are produced by agricultural soils, mainly as a result of the application of nitrogenous fertilisers. Despite previous research into agricultural N_2O emissions which has demonstrated that N_2O emissions have high spatial and temporal variability, there is still a lack of knowledge surrounding the factors that influence the magnitude of emissions from agricultural soils. Agricultural N_2O emissions for the UK's annual GHG inventory are currently estimated using a 1.25 % emission factor (EF) (to be decreased to 1 % in 2015) which assumes that 1.25 % of applied nitrogen (N) fertiliser is emitted as N_2O . The EF does not take into account influencing factors such as location or fertiliser type. Mitigation of N_2O emissions is vital if future climate change is to be prevented, yet this must also be combined with the need to intensify agricultural production to feed the increasing global population. Biochar which is a carbon rich material produced during the pyrolysis of biomass has been identified as a potentially useful soil amendment with the ability to mitigate N_2O emissions. However, most previous research has focused on laboratory scale experiments and there is a need to investigate the use of biochar in a field environment. Other N_2O mitigation options such as nitrification inhibitors, or altering fertiliser management practices, require testing under different conditions to assess their suitability for use. This thesis aims to investigate a). The factors affecting N_2O emissions from synthetically and organically fertilised arable soils, and b). To explore the potential of various N_2O mitigation options for arable systems, including biochar.

This thesis firstly investigates N_2O emissions from synthetically fertilised arable soil. Varying application rates of ammonium nitrate fertiliser were applied to a Scottish arable soil during a year long field experiment and the effects of mitigation options such as a nitrification inhibitor (DCD) were assessed. N_2O emissions were shown to be significantly affected by soil water filled pore space and the 1.25 % EF was

demonstrated to be generally greater than those calculated in this experiment. The use of DCD significantly decreased N_2O emissions and crop yields. A second year long field experiment was carried out to investigate N_2O and NH_3 emissions from an organically fertilised arable soil and to explore the effect of the timing, form and method of organic fertiliser application on emissions and EFs. Slurry, poultry litter, layer manure and farmyard manure were applied in the autumn and the spring. Cumulative N_2O emissions were generally greater from the autumn applications and NH_3 emissions were greater from the spring applications, due to wetter soil conditions and incorporation of fertiliser during the autumn. The type of fertiliser applied affected the magnitude of emissions with the greatest cumulative N_2O and NH_3 emissions from the layer manure. The method of fertiliser application had no effect on emissions. The following experiment investigated the ability of different biochars to retain N from a solution and the effect of biochar particle size on retention. A batch sorption experiment was used to test the affinity and capacity of six biochars for ammonium (NH_4^+) and nitrate (NO_3^-) from different concentrations of NH_4NO_3 solution. All of the biochars studied demonstrated the ability to retain NH_4^+ and NO_3^- from solution although greater NH_4^+ retention was observed. Differences in biochar affinity for N could be explained by pyrolysis temperature, but there was no effect of particle size or pH. Oil seed rape straw biochar was demonstrated to have the greatest NH_4^+ and NO_3^- retention capacity and as such was chosen for use in the next experiment. This work investigated the potential for oil seed rape straw biochar to decrease emissions of N_2O , CH_4 and CO_2 from stored slurry and whether any GHG mitigation effects would continue following application of the slurry to arable soil. The effect on emissions of amending the biochar and slurry mixture with DCD after application to the soil was also explored. There was no significant effect of the biochar on GHG emissions from the stored slurry although the slurry initially acted as a sink for N_2O and CO_2 . There were no significant differences between emissions from any treatments following application to the soil.

The overall results of these studies indicate that N_2O emissions are highly dependent on weather conditions, and hence location, in addition to fertiliser type and application

timing. It was concluded that the use of a standard 1.25 % EF for synthetic and organic N fertiliser applications for the whole of the UK is inappropriate. Mitigation options such as the use of DCD, altering fertiliser application season or fertiliser type have been shown to possess the potential to mitigate N₂O emissions but tradeoffs between N₂O and NH₃ emissions, and impacts on crop yields must be considered. Biochar was demonstrated to retain NH₄⁺ and NO₃⁻ ions and this property may account for biochar's N₂O mitigation capabilities as observed by previous researchers. However, if N retention is taking place, the N appears to still be available for production of N₂O and crop uptake.

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Nitrous oxide (N₂O) is a greenhouse gas which is 296 times more powerful than carbon dioxide (CO₂). In the UK approximately 71 % of N₂O emissions are produced by agricultural soils, mainly as a result of the application of nitrogen fertilisers. Although previous research has demonstrated that N₂O emissions from soil can be highly variable, there are gaps in our understanding of the factors that influence N₂O production. The UK is required to annually submit an inventory of its N₂O emissions to the EU and the UN. This requires the use of an emission factor (EF) which estimates that 1.25 % of applied nitrogen fertiliser is emitted as N₂O. This is regarded as inaccurate as it doesn't take into account any influencing factors such as location or fertiliser type. Mitigation of N₂O emissions is vital if future climate change is to be prevented, yet this must also be combined with the need to intensify agricultural production to feed the increasing global population. Potential N₂O mitigation options which require further investigation include the amendment of soil with biochar (charcoal produced specifically for soil amendment) or the use of nitrification inhibitors which prevent the production of N₂O in soil. This thesis aims to investigate a). The factors affecting N₂O emissions from fertilised arable soils, and b). To explore the potential of various N₂O mitigation options for arable systems.

These aims were achieved through field experiments to measure N₂O emissions from arable soils fertilised with a range of synthetic and organic N fertilisers. The effect of fertiliser application timing and type was investigated, in addition to the use of a nitrification inhibitor. The potential for biochar to decrease N₂O emissions from stored slurry and organically fertilised arable soil was investigated. The results indicate that N₂O emissions are highly dependent on weather conditions, and hence location, in addition to fertiliser type and application timing. It was concluded that the use of a standard 1.25 % EF for the whole of the UK is inappropriate. Mitigation options such as the use of inhibitors, altering fertiliser application season or fertiliser type have been shown to possess the potential to mitigate N₂O emissions but impacts on crop yields must be considered. Biochar was not successful at decreasing N₂O emissions although further research is required to determine the properties of biochar which may influence N₂O production.

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Chapter 1.

Introduction

1.1 Introduction

Greenhouse gas (GHG) emissions to the atmosphere and their impact on global climate are one of the greatest environmental concerns of current times. The industrialisation of nations throughout the world has caused unprecedented increases in GHG emissions and changes in climatic conditions have become evident, prompting the need for investigation into these emissions and means of reducing them. The major GHGs of concern are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Although the absolute quantity of N_2O emitted is lower than CO_2 and CH_4 , it has a global warming potential 296 times greater than that of CO_2 , making it a powerful GHG which contributes approximately 6 % to global climate change (Forster et al., 2007; Montzka, et al., 2011). Nitrous oxide also reacts with ozone in the stratosphere causing depletion of stratospheric ozone which subsequently increases the risk of harmful ultraviolet radiation reaching the earth (Pierzinski et al., 2005). The research described in this thesis focuses mainly on emissions of N_2O .

Around 40-50% of the Earth's surface is estimated to be used for agricultural purposes and hence the effects of agricultural activities have a large impact on the earth's climate (Regina et al., 2010). Agriculture is the largest anthropogenic source of N_2O , in particular agricultural soils which produce approximately 4 Tg N_2O yr^{-1} (Reay et al., 2012). Agricultural activities produce around 79% of the UK's N_2O emissions, with 90% of agricultural N_2O emissions originating from soils (DEFRA, 2011). Nitrous oxide emissions from soils mainly occur due to the use of nitrogenous fertilisers, which although crucial for food production, can cause devastating environmental impacts. Nitrogenous fertilisers may be used in an organic or inorganic form. Organic fertilisers include those such as animal manures and crop residues and inorganic fertilisers consist of manufactured N. Historically, fertiliser use was dominated by those from organic sources however the advent of industrial inorganic fertiliser production, mainly due to the Haber-Bosch process resulted in the widespread production and use of inorganic

fertiliser (Pierzynski et al., 2005). The increased use and availability of synthetic fertiliser combined with factors such as increased mechanisation of agricultural processes and increased use of pesticides has allowed agricultural production to intensify (Aneja et al., 2009). Intensification has resulted in greater food production which is necessary for the rapidly increasing global population. However, despite the food production benefits associated with increased fertiliser use, the environmental impacts of agricultural intensification have been devastating (Burney et al., 2010). Increased reactive N additions to soil (e.g. from N fertiliser) result in associated increased losses of reactive N from the soil system, through mechanisms such as N₂O emission, ammonia (NH₃) volatilization and leaching and runoff of nitrate (NO₃⁻). This causes resultant environmental issues such as climate change caused by N₂O emissions, eutrophication from NO₃⁻ leaching and acidification from NH₃ volatilisation (Lag Reid et al., 1999). Considerable effort will be needed in the future in order to sustain global food production whilst simultaneously protecting the environment.

Mitigation of GHG emissions is becoming ever more crucial, particularly due to climate change policies such as the UK Climate Change Act 2008 which commits the UK to reduce its GHG emissions by 80 % from 1990 levels by 2050 and the Climate Change (Scotland) Act 2009 which additionally commits Scotland to reduce GHG emissions by 42 % by 2020 (The Committee on Climate Change, 2014). This will be a significant challenge for agriculture, where ever increasing levels of food production are required, yet sustainability and reduced environmental impacts are also increasingly demanded. This ambition to achieve sustainable intensification is more likely to be achieved if the causes and processes underlying emissions of N₂O are thoroughly understood, as this will allow mitigation techniques to be implemented. The UK is required to annually submit an inventory of its GHG emissions, including agricultural emissions, to the EU Monitoring Mechanism (EUMM) and the United Nations Framework Convention on Climate Change (UNFCCC) (GHGI, 2014). However, quantification of N₂O emissions from agricultural soils is difficult, and measurement of emissions of N₂O from all

fertilised agricultural soil in the UK would be impossible. Therefore to compile the GHG inventory, the UK uses methods prescribed by the Intergovernmental Panel on Climate Change (IPCC) which estimate the likely magnitude of N₂O emissions. The IPCC methodology for calculating emissions involves the use of emission factors (EFs) which define the rate of emissions occurring for a given level of activity. The UK currently reports agricultural N₂O emissions using the IPCC Tier 1 EF which assumes that 1.25 % of nitrogen fertiliser applied to soil is directly emitted as N₂O (IPCC, 1996). This value has since been decreased to 1% (IPCC, 2006), however many countries including the UK do not yet use the 1% value in their N₂O inventory calculations. The Tier 1 methodology is largely regarded as being too simplistic to accurately represent the true emissions occurring and it is therefore necessary to move to the more accurate Tier 2 or Tier 3 methods if we are to gain a true picture of the UK's N₂O emissions. Moving to the higher methodology levels requires evidence of intensive measurements of N₂O emissions which can be related to various influencing factors such as geographical location or fertiliser treatment. Previous work in the UK has not fulfilled these criteria as field experiments have often used unsuitable methodologies, particularly related to minimal and un-intensive sampling regimes.

The necessity to reduce agricultural N₂O emissions has prompted research into various potential mitigation techniques. Decreasing the amount of surplus N in the soil and thereby reducing the amount of N available for production of N₂O is key to decreasing N₂O emissions. Mitigation options which operate on this principle include altering agricultural practices such as the quantity, type and timing of fertiliser application. In addition to decreasing N₂O emissions, more appropriate fertiliser application can also improve nitrogen use efficiency of the crop and may have financial benefits for the farmer associated with less loss of N from the soil system and potentially enhanced crop yields (Burton et al., 2008). Amendments such as nitrification inhibitors are another mitigation option which is currently being explored. The inhibition of the nitrification pathway of N₂O production acts to decrease N₂O emissions, and in some cases has also

increased crop yield due to improved nitrogen use efficiency (Di and Cameron, 2002). The application of biochar to soils is another potential N₂O mitigation option which is currently being investigated. Biochar is a carbon rich product produced by pyrolysis of organic material at a temperature of <700°C (Lehmann and Joseph, 2009). The mechanisms by which biochar operates to decrease N₂O emissions are poorly understood with recent research suggesting a variety of options including sorption of N in the soil (Angst et al., 2013), increasing soil aeration (Rogovska et al., 2011) and increasing soil pH (Clough and Condon, 2010). As yet, very little research into the effect of biochar on agricultural N₂O emissions has been undertaken in the field environment, and it is important to understand how biochar acts under field conditions and any limitations associated with biochar application to the soil. All potential N₂O mitigation options require careful consideration in terms of their ability to decrease N₂O emissions and any financial, environmental or health implications that may be associated with their use. The research described in this thesis includes investigation into all of the aforementioned mitigation options.

The general aims of this thesis were to improve the understanding of processes and factors affecting N₂O emissions from arable agricultural soil by undertaking intensive field experiments in addition to investigating a variety of N₂O mitigation options, in particular the use of biochar as a soil amendment. The field experiments form part of the UK's Agricultural Greenhouse Gas Research Platform which aims to improve agricultural N₂O inventory reporting by enhancing the understanding of factors affecting N₂O production and developing emission factors which reflect the range of issues affecting N₂O production across the UK (more detail provided in Appendix 1). More specific aims are described in Chapter 3.

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Chapter 2.

Scientific background

2.1 Greenhouse gases and climate change

Anthropogenic activities have been responsible for increasing emissions of the greenhouse gases (GHGs) carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) and the halocarbons into the atmosphere, resulting in changes in atmospheric concentrations of these gases and subsequently affecting the energy balance of the earth's climate system. This research focuses primarily on N₂O, but also includes CO₂ and CH₄. Greenhouse gases alter the earth's energy balance by absorbing thermal radiation which is emitted from the earth; this causes radiative heat to become trapped within the earth's atmosphere, resulting in a warming of the earth. The degree to which a GHG alters this energy balance is termed the "radiative forcing" of the gas and the combined radiative forcing of CO₂, N₂O and CH₄ is +2.47 Wm⁻² (IPCC, 2013). The global warming effect of GHG emissions can also be described using a global warming potential (GWP) value which measures the warming effect of GHG emissions relative to CO₂ over a set time period. Nitrous oxide has a GWP 296 times larger than that of CO₂, and CH₄ has a global warming potential 25 times larger than CO₂ (IPCC, 2013). Since the pre-industrial era, atmospheric concentrations of these GHGs have increased significantly, to above the natural concentration ranges (Figure 1). Between 1750 and 2011, atmospheric concentrations of CO₂ have increased from 280 to 391 ppb, largely due to increased fossil fuel use. Increases in CH₄ and N₂O concentrations are primarily due to agricultural activities and atmospheric concentrations of CH₄ and N₂O have increased from pre-industrial values of 715 ppb and 270 ppb, respectively, to 2005 values of 1803 ppb and 324 ppb respectively (IPCC, 2013).

Evidence of the impacts of increased atmospheric GHG concentrations on the world's climate are widespread. The earth's surface temperature has increased by 0.85 (+/- 0.20) °C between 1850 to 2012, and enhanced melting of glaciers and ice sheets has resulted in mean sea level rise of 0.19 (+/- 0.02) m between 1901 and 2010. Extreme weather events affecting Europe have also become more common with intense precipitation and

extreme heat events observed (IPCC, 2013). Agriculture contributes to the emission of GHGs but it is also particularly susceptible to the impacts of climate change with optimum conditions required for productive crop growth in arable agriculture. Many of the effects of climate change which have occurred in Europe such as temperature increases and increased precipitation have the potential to increase emissions of N_2O from agricultural soils, hence agriculture must adapt and endeavour to mitigate emissions in order to achieve sustainable production of food. Adaptation and mitigation activities differ in their approach to sustainable development. Adaptation to climate change can either take place in response to climate change that has already occurred or pre-empt predicted climate change effects, in comparison to mitigation activities which aim to avoid predicted future climate change (IPCC, 2007a). Both adaptation and mitigation have a vital role to play in tackling the current and future impacts of climate change and minimising the effects of climate change on society.

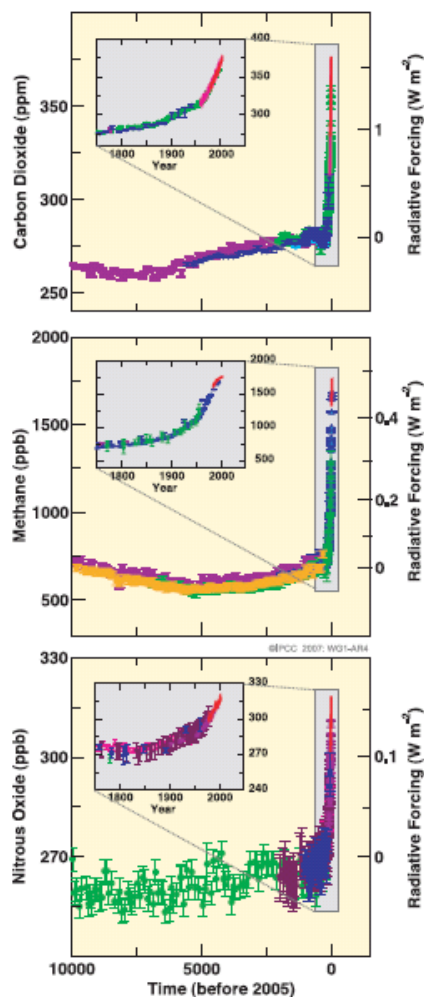


Figure 1. Changes in atmospheric greenhouse gas concentrations over the last 10,000 years (IPCC 2007b)

2.2 The global and soil nitrogen cycles

Nitrogen (N) is essential for life on Earth. Around 98% of the Earth's N is stored in the lithosphere however the dynamic nature of N means that it is easily transferred to alternative locations such as the hydrosphere, atmosphere and biosphere. These transformations are referred to as the global N cycle. 78 % of the atmosphere consists of N₂ which is a relatively unreactive gas (Laegreid et al., 1999), however, the addition of reactive N to the atmosphere results in atmospheric impacts including global warming caused by N₂O, acid rain, smog and destruction of atmospheric ozone (Pierzynski et al., 2005). The definition of reactive N is “all biologically active, photochemically active and radiatively active N compounds in the atmosphere and biosphere of the earth” and includes NH₃, NH₄⁺, N₂O and urea. Subsequent deposition of reactive N to terrestrial or aquatic environments may result in damage through acidification and/or eutrophication (Laegreid et al., 1999).

An important part of the global N cycle is the soil N cycle. The soil N cycle is vital for human life on earth as N is essential for plant growth. N deficiency results in limited plant development and therefore appropriate levels of soil N are vital for successful agricultural practices (Laegreid et al., 1999). The soil N cycle consists of a range of processes and transformations which convert N to a variety of forms. The main natural inputs to the soil N cycle are by N fixation, atmospheric deposition and weathering and decomposition (Pierzynski et al., 2005). N fixation takes place either by biological processes or lightning (Mosier, 2001). Increased additions of reactive N to the soil N cycle have occurred over the past 40 years due to increasing biological fixation related to crop production, fossil fuel use and use of synthetic N fertiliser (Mosier, 2001).

2.3 Nitrous oxide production in agricultural soils

The application of N fertiliser to agricultural soil in the form of either synthetic or organic fertilisers causes a temporary surplus of ammonium (NH_4^+) and nitrate (NO_3^-); this surplus is responsible for the subsequent production of N_2O as a byproduct of the microbial processes of nitrification and denitrification (Figure 2) (Chapuis-Lardy et al., 2007; Inselbacher et al., 2011). These processes may occur separately or simultaneously, making it difficult to quantify the proportion of N_2O emitted which is associated with each process (Bateman and Baggs, 2005). Nitrification is the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-) via nitrite (NO_2^-) and N_2O is produced as a byproduct of the reactions (Wrage et al., 2001). Nitrification is an autotrophic process carried out by microorganisms including *Nitrosomonas* sp., and *Nitrobacter* sp., under aerobic conditions (Clough et al., 2007). Denitrification is the reduction of NO_3^- to dinitrogen (N_2) via N_2O and is a heterotrophic process which takes place under anaerobic conditions (Flechar et al., 2007; Toyoda et al., 2011). Nitrification and denitrification represent important sources of microbial energy. The microorganisms which carry out these transformations have evolved to use inorganic N in their electron transport systems or respiratory chains. The inorganic N is used to provide electrons, or in the case of denitrification which takes place under O_2 limited conditions, as a terminal electron acceptor during this process. The biochemical N cycle therefore provides energy for the soil microbial community but simultaneously produces N_2O (Williams et al. in press). In addition to nitrification and denitrification, other N_2O producing processes have been identified as important in contributing to N_2O fluxes from soils. Nitrifier denitrification is regarded as a considerable mechanism by which N_2O is produced and involves the reduction of NO_2^- to N_2 via N_2O by autotrophic NH_3 oxidising bacteria (Wrage et al., 2001; Toyoda et al., 2011). Non biological chemodenitrification, aerobic denitrification and fungal denitrification are also regarded as important N_2O production processes within the soil environment (Flechar et al., 2007). Nitrate ammonification is also a considerable N_2O source which involves the respiration of NO_3^- to NH_4^+ via NO_2^- by bacteria under anoxic conditions, with N_2O production being a byproduct of the

reaction. Nitrate ammonification may take place concurrently with denitrification, and as such it is unknown how large the contribution of nitrate ammonification to N_2O production in soils may be (Streminska et al. 2011).

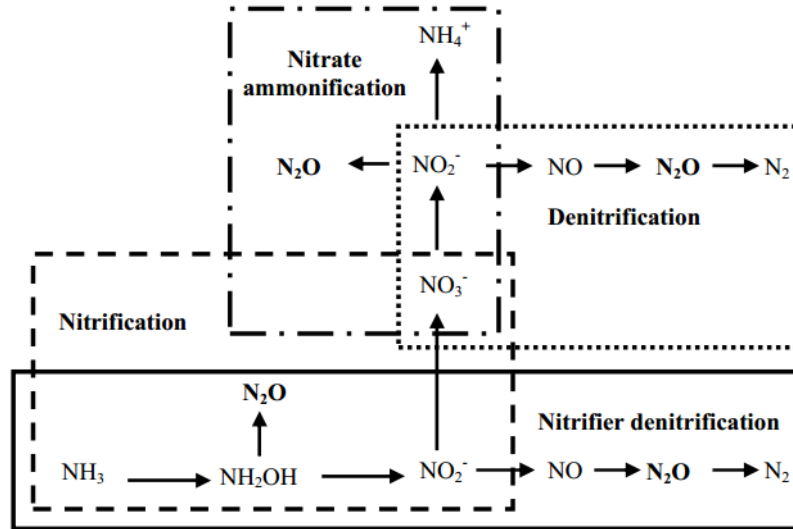


Figure 2. Microbial sources of N_2O in the soil (adapted from Baggs, 2008).

The processes responsible for the production, or consumption, of N_2O by soils are strongly influenced by a variety of soil conditions, which results in high spatial and temporal variability of N_2O fluxes (Lilly et al., 2003) and subsequent difficulty in accurately assessing the magnitude of fluxes (Rafique et al., 2012). Soil water filled pore space (WFPS) is regarded as the most influential variable affecting N_2O fluxes from agricultural soils (Castellano et al., 2010) due to its control over soil aeration and O_2 content, both of which are crucial in determining the contribution of nitrification and denitrification to N_2O production. N_2O production is an exponential or positive linear function of WFPS (Castellano et al., 2010) with maximum N_2O emissions occurring at 50-70% WFPS (Flechar et al., 2007). Although values vary, it is generally suggested that denitrification is the dominant N_2O producing process at >60 % WFPS, although in water logged soils over 90 % WFPS, N_2O flux decreases as N_2O is reduced to N_2 (Smith et al., 1998). At <60 % WFPS, nitrification is considered to dominate the production of

N₂O (Bateman and Baggs, 2005). Despite greater production of N₂O at higher WFPS due to enhanced denitrification, whether the N₂O is eventually released from the soil depends on the source area of N₂O production. If the source region is an anaerobic microsite in a mostly aerobic soil then the N₂O molecule may diffuse into an oxygenated pore and be emitted from the soil, however, if it is produced far below a clod of saturated soil it may instead be reduced to N₂ before being emitted (Smith et al., 2003). Soil compaction is an important factor which determines the dominance of nitrification or denitrification in the soil due to the resultant impacts on soil aeration. The reduction in soil porosity caused by compaction, leads to subsequent increases in the quantity of anaerobic soil due to increased WFPS and decreased O₂ diffusion. This results in enhanced denitrification and N₂O production (Bessou et al., 2010). Soil temperature and pH also determine the magnitude of N₂O fluxes. There is an exponential relationship between soil temperature and N₂O production, due to the development of anaerobic microsites in the soil as temperature increases causing a resultant increase in denitrification (Smith et al., 2003). The optimum pH range for nitrification and denitrification is pH 6-8 (Pierzynski et al., 2005). The variety of processes responsible for the production, or consumption, of N₂O by soils are strongly influenced by soil conditions, which results in high spatial and temporal variability of N₂O fluxes (Lilly et al., 2003) and subsequent difficulty in accurately assessing the magnitude of fluxes (Rafique et al., 2012).

Soils are generally considered to be a source of N₂O, however they may sometimes act as temporary sinks, often in soils with high moisture contents and low mineral N. The consumption of N₂O by nitrifiers during nitrifier denitrification and the reduction of N₂O to N₂ during denitrification are suggested to be responsible for this (Chapuis-Lardy et al., 2007). Evidence of N₂O consumption in soil (i.e. negative N₂O fluxes) has been reported in various studies; Smith et al. (1998) reported small negative N₂O fluxes from fertilised grassland and spring barley experimental sites, and Butterbach-Bahl et al. (1998) and Jordan et al. (1998) both reported negative N₂O fluxes from forest

ecosystems. Despite the evidence for consumption of N_2O by soils, focus is generally concentrated on the higher, and more evident, production rates of N_2O (Chapuis-Lardy et al., 2007).

2.4 Carbon dioxide and methane emissions from agricultural soils

Although this thesis focuses mainly on agricultural N₂O emissions, it is important to take into account emissions of other GHGs from agricultural soils, and elsewhere, these being CO₂ and CH₄ (Johnson et al., 2007) as their emissions are often closely interlinked. Figure 3 shows the contribution of various aspects of UK agriculture to GHG emissions. The relationships between these gases must be considered if activities to decrease emissions of one gas are not to unintentionally increase those of another. The balance between sinks and sources of these GHGs must also be understood if we hope to decrease net GHG emissions. Schulze et al. (2009) reviewed estimates of European CO₂, CH₄ and N₂O emissions from 2000-2005 and determined that despite considerable CO₂ fluxes from industrialized areas, CH₄ fluxes from animal agriculture and peatlands and N₂O fluxes from intensive croplands and grasslands, Europe's GHG balance is currently neutral. This due to extensive carbon sequestration in grasslands and forested areas. However, the current intensification of agriculture suggests that Europe is likely to become a net source of GHGs in the future, making land management a vital area of GHG mitigation potential (Schulze et al., 2009).

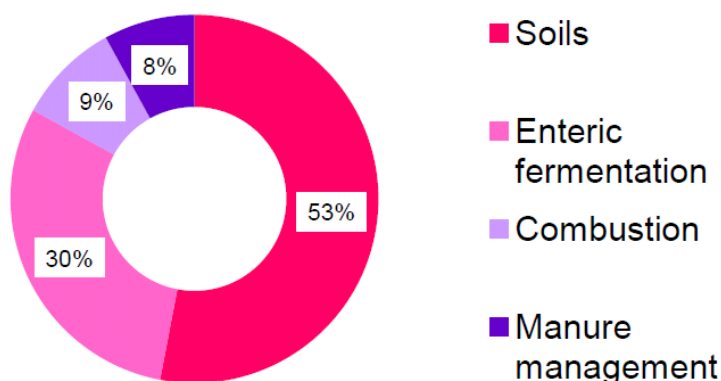


Figure 3. UK agricultural GHG emissions by source (POST, 2014)

Soils play an important role in the global C cycle, representing one of the largest pools of C. Photosynthesis by plants results in the fixation of atmospheric CO₂, however CO₂ can be returned to the atmosphere as a result of respiration by plant roots and shoots and also during decomposition of the plant by soil micro-organisms (Pierzynski et al., 2005), although between 10-20% of plant C content is retained by the soil as organic matter following decomposition. Conversion of natural environments to agricultural land is a large source of CO₂ emissions from soils and it is estimated that over approximately the last 150 years, this has been responsible for around one third of anthropogenic CO₂ emissions (Foley et al., 2005). In addition, agricultural practices such as soil tillage, and resultant impacts such as soil erosion, represent a threat to soil C stability, with soil erosion potentially resulting in an annual release of 1 Gt C to the atmosphere (Ball et al., 1999, Johnson et al., 2007, Pierzinski et al., 2005). Agricultural activities such as nitrogen fertilisation, in addition to increasing soil N₂O emissions, may also act to increase soil CO₂ emissions due to increased root respiration caused by rapid plant growth (Inselbacher et al., 2011). The application of nitrogen fertilisers, in particular organic fertilisers which also contain large amounts of C must be carefully managed as the C:N ratio of the soil may influence loss of N from the soil system. A high ratio of C to N in the soil promotes microbial growth and may enhance immobilisation of mineral N. However, if amendments with a very high C:N ratio (>30:1) are applied to the soil, excessive growth of microbial biomass and N immobilization can occur, resulting in crop N deficiency. A lower soil C:N ratio and subsequently less microbial growth may lead to excess mineral N concentrations in the soil, increasing the likelihood of loss of N from the soil in the form of N₂O or through leaching. This may occur when amendments with a low C:N ratio such as poultry manure are applied to the soil (Pierzinski et al., 2005).

Agricultural activities are suggested to account for around 44 % of the UK's total CH₄ emissions. (Defra, 2011) The majority of agricultural CH₄ emissions are produced by methanogenesis, during which organic matter is broken down to form methane by

microorganisms during the respiration process. Methanogenesis takes place under anaerobic conditions in soils, during ruminant livestock enteric fermentation and manure management (Cloy et al., 2012; Johnson et al., 2007; Pierzynski et al., 2005). Although soils may act as a CH₄ source this is dependent on soil moisture with drier soils acting as a CH₄ sink due to metabolization of CH₄ by soil methanotrophic bacteria. (Johnson et al., 2007).

2.5 Nitrous oxide mitigation options

Increasing levels of N₂O in the troposphere and the expected impact of future global climate change make mitigation of agricultural N₂O emissions a necessity. However, the world's population is expected to increase to a peak of 9.22 billion by 2075 (UN, 2004), placing more demands on food production and supply, particularly due to the demand for more resource intensive food products (Garnett et al., 2013). The requirement to increase food production to satisfy the growing population and to maintain food security, makes agricultural intensification an urgent requirement. Agricultural practices can often be linked to environmental degradation, including production of GHGs and it is desirable to decrease the environmental impacts of agriculture. Sustainable intensification of agriculture has been suggested as a means by which food production may be increased, whilst simultaneously decreasing negative environmental impacts thereby allowing both aims to be achieved (Garnett et al., 2013; Thomson et al., 2012). The work in this thesis investigates all of the N₂O mitigation options described below, due to their identification as key measures by which N₂O emissions from agricultural soils may be decreased (Johnson et al., 2007; Rees et al., 2013). Although other N₂O mitigation options such as land drainage and biological N fixation have also been identified as potentially important (Rees et al., 2013), the scope of this project was not wide enough as to also include investigation into these measures

Potential means by which N₂O emissions from agricultural soils could be reduced include alteration of fertiliser management practices by increasing efficiency and reducing excess N applied to the soil (Burney et al., 2010). Appropriate timing of fertiliser application is crucial, due to the N requirements of the growing crop and the environmental conditions which may affect N₂O production. Ball et al. (1999) noted smaller emissions of N₂O from soil to which N fertiliser had been applied whilst the crop was actively growing, compared to that in which the crop mineral N requirement was low. A suggested means by which fertiliser may be applied at more appropriate

times, involves splitting the application of fertiliser into a few smaller doses, instead of a single large application. Smaller doses of fertiliser are generally more adequately suited to crop requirements in addition to decreasing the risk of excess N in the soil and potential loss of N from the system (Burton et al., 2008). The type of N fertiliser applied, for example urea or ammonium nitrate, has also been shown to have an effect on the magnitude of N₂O emissions. Some research has indicated that applications of urea result in lower N₂O emissions than applications of ammonium nitrate (Dobbie and Smith, 2003; Smith et al., 2012), although this effect appears dependant on other variables including the timing of application and soil moisture. Ammonia emissions, which are believed to be higher from urea than ammonium nitrate, must also be taken into account (Clayton et al., 1997; Dobbie and Smith, 2003; Smith et al., 2012).

There is also potential for mitigation of N₂O emissions when using organic fertilisers, such as slurries or solid manures. The storage of these fertilisers, particularly slurry, often occurs over long periods of time prior to field application and is a considerable source of CH₄ due to the degradation of organic matter by bacteria under anaerobic conditions, in addition to producing CO₂, N₂O, and NH₃ (Misselbrook et al., 2005; Sommer et al., 2007). The need to decrease GHG emissions from stored slurry has led to research into the potential for amendment of the slurry with materials that form a slurry “crust” such as straw, leca pebbles and biochar, in addition to natural crust development, all of which have successfully decreased GHG emissions although on a smaller scale than would be practiced in reality (Angst et al., 2013a; Misselbrook et al., 2005; Sommer et al., 2000).

The application of organic fertilisers to soil is also a source of CH₄, N₂O and NH₃, in addition to CO₂ which is released during C turnover. This thesis focuses particularly on N₂O and NH₃ emissions. The production of these gases during organic fertiliser storage and also following application represents not just an environmental concern, but also a

financial loss for the farmer due to potential negative impacts on crop yield related to lower nutrient availability in the fertilisers. The form of organic fertiliser applied has been shown to affect the magnitude of emissions of N_2O and NH_3 with properties of the fertiliser such as the readily available N content and moisture content being particularly important. Large readily available N contents such as those found in poultry manures increase the risk of N loss via leaching or as N_2O or NH_3 . Slurries tend to have high moisture contents in comparison to other organic fertilisers and this can increase the risk of N_2O emissions following fertilisation due to greater denitrification in the soil (Defra, 2010; Jorgensen et al., 1998). The timing of organic fertiliser application has also been shown to affect the magnitude of N_2O and NH_3 emissions with greater emissions of NH_3 generally occurring in dry and warm conditions, however greater N_2O emissions often occur under wet conditions (Flechard et al. 2007; Meisinger and Jokela, 2000). The method of organic fertiliser application may also affect emissions of N_2O and NH_3 . Placement of organic fertilisers within the soil, instead of on the soil surface has been shown to decrease NH_3 emissions (Wulf et al., 2001), however, this has also been associated with enhanced N_2O emissions (Peral et al., 2006) due to increased soil moisture contents and denitrification rates.

The application of Nitrification Inhibitors to soils is regarded as another potential means of decreasing N_2O emissions (Clough et al., 2007). Nitrification inhibitors act to inhibit the oxidation of NH_4^+ to NO_3^- during nitrification (Di and Cameron, 2002) through deactivation of the ammonia monooxygenase enzyme used in the primary stage of nitrification (Amberger, 1989). The nitrification inhibitor Dicyandiamide (DCD) has effectively demonstrated the potential for reduction in N_2O emissions from soils; mean reductions of 77 % and 70 % respectively were achieved from a simulated grazed grassland (Di and Cameron, 2003) and from urine patches on grazed grassland of four different soil types in New Zealand (Di et al., 2007).

2.6 Biochar

Biochar can be defined as “the carbon rich product produced by so-called thermal decomposition of organic material under limited supply of oxygen (O_2) and at relatively low temperature ($<700\text{ }^{\circ}C$)” (Lehmann and Joseph, 2009). Biochar differs from charcoal, in that biochar is defined as being produced with the purpose of being applied to soil (Lehmann and Joseph, 2009). Biochar is very stable in soil due to its composition of C in a highly recalcitrant chemical form (Shackley and Sohi, 2010). The stability of biochar results in its ability to sequester C for timescales of up to thousands of years (Fowles, 2007). Application of biochar in order to enhance C storage has been practiced historically in some areas of the world. The Terra Preta soils in the Amazon Basin contain high quantities of total C due to the deliberate application of biochar and as a result of biomass burning by Amerindian populations thousands of years ago. The remaining high C stocks in these soils even after this amount of time represent considerable evidence of the effectiveness of biochar at sequestering C (Lehmann et al., 2006). In addition to sequestering C, biochar application offers other benefits to the soil environment. It has the ability to retain nutrients and to improve other aspects of soil physics and biology such as improving soil structure, aeration, water holding capacity and providing microsites that attract soil microbes (Johnson et al., 2007; Lehmann et al., 2006), resulting in increased soil fertility (Koide et al., 2011). The enhanced nutrient use efficiency of plants associated with the use of biochar also reduces leaching of nutrients to water courses thereby reducing environmental pollution (International Biochar Initiative, 2012). In addition to sequestering C in soils, recent research has demonstrated that biochar may have the ability to mitigate emissions of N_2O from agricultural soils.

The retention of NH_4^+ and NO_3^- by biochar is of particular interest due to the links between this and reduction in N_2O emissions. Biochar has a predominantly negative surface charge and hence a high cation exchange capacity (CEC), allowing retention of cations such as NH_4^+ to take place. The cation retention capacity of biochar is suggested

to increase as the biochar ages and is oxidised (Cheng et al., 2006). The ability of biochar to remove NH_4^+ and NO_3^- ions from nutrient solutions was shown by Yao et al. (2012) who demonstrated removal of NO_3^- and NH_4^+ from solution by biochars made from a range of different feedstocks, although greater removal of NH_4^+ than NO_3^- took place. The retention of NO_3^- or NH_4^+ by biochar can also be demonstrated by a reduction in leaching of these nutrients from soil following biochar addition. Yao et al. (2012) found a 34 % decrease in NO_3^- leaching following addition of biochar to soil in a column experiment and a 5 % reduction in NO_3^- leaching was found by Kameyama et al. (2012) following biochar amendment of soil in a column experiment. However, no effect on NO_3^- leaching and for one treatment an increase in NO_3^- leaching was reported by Singh et al. (2010) when wood and poultry manure biochars were applied to fertilised soil columns. The contradictory results obtained in these experiments relating to the effect of biochar on NO_3^- leaching from soil has been suggested to be due to weak adsorption of NO_3^- by biochar due to its low anion exchange capacity which also decreases over time, and subsequent easy desorption of the NO_3^- (Kameyama et al., 2012 ; Singh et al. 2010). Leaching of NH_4^+ from soils has also been shown to reduce following biochar amendment. Ding et al. (2010) found a decrease in leaching of NH_4^+ from biochar amended soil columns of 15 % after a 70 day soil column experiment. A significant decrease in NH_4^+ leaching was also found by Lehmann et al. (2002) during a lysimeter study applying biochar to Amazonian soils and by Angst et al. (2013b), who suggested that the decrease in leached NH_4^+ was due to sorption of NH_4^+ onto negatively charged biochar surfaces.

The application of biochar to soils has been shown to decrease N_2O emissions, with most evidence for this coming from laboratory based experiments although some field experiments have taken place. Suppression of N_2O emissions has been noted from laboratory experiments using a range of biochars made from feedstocks including mixed hardwood, brush, hickory, sawdust, biowaste, sycamore applied to a range of soils including those from grassland and fields sown with wheat, corn, soybean or

miscanthus. Fertilisers have ranged from commercial inorganic fertilisers to organic manures and slurries (Angst et al., 2013b; Case et al., 2012; Cayuela et al., 2013; Rogovska et al., 2011; Spokas et al., 2009; Yanai et al., 2007). There have been fewer field experiments, however the observed effects of biochar on N₂O emissions have generally been promising and have occurred in a range of field environments. Felber et al. (2014) applied greenwaste biochar to meadow soil and successfully decreased N₂O emissions by 22 %. However, when the same experiment was carried out under laboratory conditions, up to 58 % decrease in N₂O emissions was seen from the biochar amended soil. Felber et al. (2014) suggested that this difference was due to greater mixing of the biochar and soil in the laboratory incubation causing enhanced retention of NO₃⁻. Taghizadeh-Toosi et al. (2011) found a 70 % reduction in N₂O emissions from bovine urine patches following application of biochar to soil and Liu et al. (2012) found a significant decrease in N₂O emissions from wheat straw biochar amended rice paddy soil. In contrast, Scheer et al. (2011) observed no decrease in N₂O emissions following application of cattle feedlot biochar to subtropical pasture. A search of the literature was conducted for all experiments in which biochar has been applied to soil in the field or laboratory to study the effect on N₂O emissions. The biochar feedstock, soil type and effects observed on N₂O emissions from each study are reported in Table 1.

Authors	Biochar feedstock	Laboratory or field study	Soil type	Effects observed
Singh et al. (2010)	Wood and poultry manure	Laboratory	Alfisol and Vertisol	Decreased N ₂ O emissions
Angst et al. (2013b)	Sycamore	Laboratory	Cambic Arenosol	Decreased N ₂ O emissions
Case et al. (2012)	Mixed hardwood	Laboratory	Sandy loam	Decreased N ₂ O emissions
Van Zweiten et al. (2010)	Greenwaste, poultry litter, papermill waste, biosolids	Laboratory	Ferrosol	Decreased N ₂ O emissions
Rogovska et al. (2011)	Mixed hardwood	Laboratory	Clarion	Decreased N ₂ O emissions
Spokas et al. (2009)	Mixed sawdust	Laboratory	Waukegan silt loam	Decreased N ₂ O emissions
Spokas and Reicosky (2009)	Corn stover, peanut hulls, macadamia nut shells, wood chips, turkey manure plus wood chips, coconut shell	Laboratory	Waukegan silt loam	Decreased N ₂ O emissions for all biochars, except compost amended biochar which increased N ₂ O emissions
Yanai et al. (2007)	Municipal biowaste	Laboratory	Typic Hapludand,	Decreased N ₂ O emissions
Felber et al. (2014)	Greenwaste	Field and laboratory	Stagnic Cambisol	Decreased N ₂ O emissions (greater reduction in laboratory than field experiment)
Taghizadeh- Toosi et al. (2011)	Monterey Pine	Field	Templeton silt loam	Decreased N ₂ O emissions
Scheer et al. (2011)	Cattle feedlot waste	Field	Ferrosol	No effect on N ₂ O emissions
Brunn et al. (2011)	Wheat straw	Laboratory	Loamy soil	Biochar applied on its own increased N ₂ O emissions, biochar applied with slurry decreased N ₂ O emissions
Jia et al. (2012)	Maize straw	Laboratory	Fimi-Orthic Anthrosols	Decreased N ₂ O emissions
Kamman et al. (2012)	Hull, maize, wood chip	Laboratory	Luvisol	Decreased N ₂ O emissions
Liu et al. (2012)	Wheat straw	Field	Unknown	Decreased N ₂ O emissions
Zhang et al. (2012)	Wheat straw	Field	Stagnic Anthrosol	Decreased N ₂ O emissions
Sarkhot et al. (2012)	Mixed hardwood	Laboratory	Typic Haploxeralfs	Decreased N ₂ O emissions
Stewart et al. (2012)	Oak	Laboratory	Aridic Argiustoll, Oxyaquic Hapludalf, Aeric Haplaquept, Aquic Haplustoll	Decreased N ₂ O emissions
Troy et al. (2013)	Anaerobically digested pig manure, Sitka spruce	Laboratory	Acid brown earth	Increased N ₂ O emissions

Table 1. Overview of the experiments currently reported in the literature investigating the effect of biochar on N₂O emissions.

Numerous mechanisms have been suggested to account for the N₂O suppressive abilities of biochar. Retention of NH₄⁺ by sorption to the negatively charged biochar surface, thereby reducing the potential for nitrification of NH₄⁺ to take place in the soil, has been proposed by some authors (Angst et al., 2013b; Clough et al., 2010; Felber et al., 2014; Taghizadeh-Toosi et al., 2011). Retention of NO₃⁻ by the biochar thereby reducing denitrification has also been suggested as a potential mechanism. Proposed means by which NO₃⁻ may be retained by the biochar include through anion exchange (Kameyama, 2012), retention in solution in biochar pores (Prendergast-Miller et al. (2011), or cation-bridge bonding (Mukherjee, 2011). The retention of NH₄⁺ and NO₃⁻ would account for decreased rates of nitrification and denitrification as observed by Clough et al. (2010) and Taghizadeh-Toosi et al. (2011). Alteration of soil physical properties including soil aeration and bulk density by biochar has also been suggested to be responsible for suppression of N₂O emissions (Rogovska et al., 2011; Van Zweiten et al., 2010; Yanai et al., 2007), although Case et al. (2012) suggested that increased aeration of the soil by biochar may only have a minimal impact on N₂O emissions and was not the only mechanism responsible. The high ash content of biochar and associated alkalinity causes soil pH to increase following biochar addition. This increase in pH has been proposed to decrease denitrification or to convert N₂O to N₂ during the denitrification pathway (Clough et al., 2010; Van Zweiten et al., 2010), however this mechanism has been disputed by Yanai et al. (2007). Cayuela et al. (2013) suggested that biochar decreases N₂O emissions by acting as an “electron shuttle”, helping to move electrons to N₂O reducing bacteria, and thereby increasing the reduction of N₂O to N₂.

2.7 Nitrous oxide emission factors

The Intergovernmental Panel on Climate Change (IPCC) methodologies for estimating agricultural GHG emissions are currently used by the UK when reporting GHG emissions annually to the EU Monitoring Mechanism (EUMM) and the United Nations Framework Convention on Climate Change (UNFCCC). Submissions to the EUMM and UNFCCC take the form of a national N₂O inventory report and tables of N₂O emissions from source sectors (NAEI, 2014). Despite the complexity surrounding the processes responsible for N₂O emissions from agricultural soils, the UK and many other countries which do not possess sufficient quality of measurements of agricultural N₂O emissions are currently required to estimate direct emissions of N₂O from agricultural land in the UK. Estimations take place using the IPCC Tier 1 methodology for calculating emission factors (EF) which assumes that N₂O emissions equal 1.25 % of applied N fertiliser (IPCC, 1996). The 1.25 % EF was used as the default EF following a review of published N₂O emissions from agricultural soils by Bouwman (1996) who determined that a 1.25 % EF was an appropriate means of equating the amount of fertiliser applied, to the quantity of N₂O emitted, regardless of fertiliser type. The default Tier 1 EF has more recently been decreased to 1 % (IPCC, 2006), however this value has not yet been adopted by many countries, including the UK. The Tier 1 approach does not take into account variations in factors which affect N₂O emissions such as soil type, climate, land use or management practices and therefore an EF of 1 % is assumed to be constant across the UK (Giltrap et al., 2010). This results in high levels of uncertainty regarding national N₂O inventories, particularly due to the large spatial and temporal variabilities associated with N₂O emissions. Despite the use of this method, actual measured N₂O emissions across the UK have shown much deviation from this default value of 1 %, particularly in Scotland, due to differences in climatic conditions compared to the rest of the UK. N₂O EFs calculated for Scottish agricultural soils by Clayton et al. (1997) and Dobbie et al. (1999) ranged from 0.2-7 %. This variability in EFs compared to the standard UK EF of 1.25 % is suggested to be largely due to intense short term weather systems in Scotland resulting in large changes in soil WFPS (Dobbie et al., 1999).

Alternative IPCC methods of calculating N₂O emissions for national inventories are “Tier 2” and “Tier 3” methods. Countries may use the Tier 2 method if they possess more detailed activity data including climate, land use and crop type which can be taken into account when estimating emissions, resulting in more accurate and detailed emissions reports. Tier 3 methods involve a modelling approach to estimate N₂O emissions, which has been validated by experimental measurement data (IPCC, 2006). The UK aims to move towards a Tier 2 or Tier 3 approach, which will be achieved by obtaining a greater understanding of the processes and factors affecting agricultural N₂O emissions through experimental and modelling approaches.

Indirect emissions of N₂O can also be estimated in a similar way to direct emissions, with categorization into Tier 1, 2 and 3 methodologies. Indirect emissions of N₂O from agricultural soils can take place via two pathways; firstly due to volatilization of applied N as NH₃, which may then be deposited as NH₄⁺ or NO₃⁻ in aquatic or terrestrial ecosystems, after which transformation of NH₄⁺ and NO₃⁻ to N₂O may occur. Secondly, N, usually in the form of NO₃⁻, may be leached from the soil or transported in runoff waters to aquatic environments where nitrification or denitrification to N₂O may take place. The Tier 1 default EFs for volatilization of NH₃ from applied synthetic or organic fertiliser accounts for 10 % and 20 % respectively of the total amount of N applied, however the indirect N₂O emissions associated with volatilization and redeposition of N are only 1 % of the volatilized NH₃-N. An emission factor of 30 % is used to estimate the amount of applied N lost during leaching or runoff, although only 0.75 % of this leached or runoff N is associated with indirect N₂O emissions (IPCC, 2006). If the direct and indirect sources of N₂O emissions from applied fertiliser N are combined, this produces an estimate of 1.33-1.43 % of applied N being emitted as N₂O (Cloy et al., 2012). There is uncertainty associated with estimated calculations of indirect N₂O emissions from a country, as N which is volatilized or runoff, may not be deposited in the source country, potentially leading to errors in emission estimations (IPCC, 2006).

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Chapter 3.

Overview of thesis

3. Overview of thesis

This thesis involved a combination of fieldwork carried out at two arable agricultural sites and laboratory work, using soils collected from these sites, or biochar. The main aims of this thesis were to a). Improve the understanding of the soil processes and climatic and environmental factors affecting N₂O emissions from fertilised arable agricultural soils, which will ultimately improve the accuracy of the UK's agricultural N₂O EFs and N₂O inventory. b). To investigate the effectiveness of a range of potential N₂O mitigation options, including biochar, for arable agricultural soils. To achieve these aims, four experiments were carried out and the thesis is composed of four chapters describing this work, which are structured in the form of scientific papers designed for publication.

The first results chapter (Chapter 5) describes the work carried out at Gilchriston farm to investigate the effects of a range of synthetic fertiliser treatments on N₂O emissions, emission factors and emission intensities from a Scottish arable agricultural soil planted with spring barley, measured over 12 months. Treatments applied included ammonium nitrate fertiliser (40-200 kg N ha⁻¹) and urea fertiliser (120 kg ha⁻¹). The effect on N₂O emissions of varying fertiliser chemical form, quantity, application timing and use of a nitrification inhibitor (DCD) were investigated. N₂O emissions were measured from 15 static closed chambers per treatment using an intensive sampling regime, in addition to measuring soil properties, weather conditions, crop yield and crop N uptake. This research formed part of the UK Agricultural Greenhouse Gas Research Platform's activities (more details provided in Appendix 1).

Arable agricultural soils may be fertilised with either synthetic or organic fertiliser. To improve our understanding of N₂O emissions from arable agricultural soils it was therefore necessary to also investigate N₂O emissions from organic fertilisers at Boghall

farm, near Edinburgh. This allows comparison between N₂O emissions from synthetic and organically fertilised soils. Chapter 6 describes the work carried out at Boghall farm to investigate the effects of fertiliser application season, type, incorporation and method on emissions of N₂O and NH₃ from a range of organic fertiliser treatments applied to a Scottish arable agricultural soil planted with winter wheat. The effects of each treatment on N₂O and NH₃ emission factors in addition to crop yield and N uptake were also assessed. Fertilisers included cattle slurry, farm yard manure, poultry litter and layer manure, all of which were applied at the recommended rates which varied from (50-244 kg N ha⁻¹). The slurry was applied using two different methods, either surface broadcast application or trailing hose application. This experiment was composed of two separate experiments to assess the effect of fertiliser application timing on N₂O and NH₃ emissions, and as such applications were made in October 2012 and April 2013. After each set of applications NH₃ emissions were measured for two weeks using wind tunnels and N₂O emissions were measured for 12 months using static closed chambers. The ancillary measurements made for the experiment described in Chapter 5 were replicated for this experiment, with the addition of soil leachate measurements to assess leaching of N from the soil (results not included in this thesis). This experiment also formed part of the UK's Agricultural Greenhouse Gas Research Platform (see Appendix 1).

Following Chapter 6, the thesis then moves on to work carried out regarding the use of biochar as a potential N₂O mitigation option. Although the work described in Chapter 7 is a stand alone experiment, it also forms the preliminary work for Chapter 8. Chapter 7 describes a laboratory experiment carried out to assess the ability and capacity of different biochars to retain NO₃⁻ and NH₄⁺ through a batch sorption experiment. The relationship between the extent of N sorption and biochar properties including pH and pyrolysis temperature were assessed. Six biochars were tested from the following feedstocks and produced at pyrolysis temperatures of between 450°C- 550°C: Miscanthus straw (produced from two different slow pyrolysis facilities), oilseed rape straw, willow, mixed softwood, mixed hardwood. Two particle sizes of biochar were

tested, these were <1 mm and 1-4 mm, to enable investigation of potential effects of biochar particle size on N retention. The batch sorption experiment used ammonium nitrate (NH_4NO_3) solutions at concentrations of: 0, 25, 50, 75, 100 mg $\text{NH}_4\text{NO}_3 \text{ L}^{-1}$ to which biochar was added at a solid-to-liquid ratio of 1:150. The Initial Mass Isotherm Approach was used to define removal or release of NO_3^- and NH_4^+ from the solution by the biochars. This work was a preliminary experiment to the work described in Chapter 8 as it enabled identification of the biochar with the greatest N retention capacity to use in the following slurry storage and field experiments.

Chapter 8 follows on from Chapter 7 by using the biochar which was shown to have the greatest N retention capacity in Chapter 7 (the oilseed rape straw biochar). Chapter 8 focuses on the use of biochar in farm systems, by assessing the potential for biochar to decrease GHG emissions (N_2O , CO_2 and CH_4) from stored slurry and then from slurry amended arable soil at Boghall farm. Additionally, the potential for a combination of a nitrification inhibitor (DCD), slurry and biochar to reduce N_2O emissions from soil is assessed. Cattle slurry was stored in 12 tanks (300 L of slurry in each) and 19 kg of oilseed rape straw biochar was applied to 6 of these tanks, the others were left as “control” treatments. Emissions of CO_2 , CH_4 and N_2O from the tanks were measured 15 times over the 50 day storage period. The contents of the tanks were then applied to arable soil in the field environment. The treatments that were applied to the soil were: Slurry only, slurry + biochar and slurry + biochar + nitrification inhibitor (DCD). The effects of the treatments on crop yield were also assessed. The field experiment carried out in Chapter 8 complements the field experiment carried out in Chapter 6, as both experiments were carried out at the same location and using the same control treatments, allowing comparison between both experiments to be made. Emissions of CO_2 , CH_4 and N_2O from the biochar field experiment were measured for 12 months following application using the static closed chamber technique.

In addition to the aforementioned experimental work, development of some of the methodologies used also took place. It was decided to include this work in the appendices as although it was important in enabling successful completion of the experimental work, it does not contribute directly to the overall aims of the thesis. The chambers used for measuring N₂O emissions in the work described in this thesis did not include fans to mix the headspace air. The inclusion of fans in chambers is a controversial issue, mainly due to the lack of available evidence either supporting or refuting the use of fans. It was therefore decided to conduct an experiment to assess the effect of the use of fans in chambers on measured N₂O emissions. This experiment, which is described in Appendix 2, took place after the first field experiment had ended, however the findings of this experiment were used to inform chamber design in the subsequent field experiments. Methodological development also took place during the work described in Chapter 7 to evaluate the use of autoclaving as a means of sterilising biochar and was a vital part of the batch sorption experiment. This work is described in Appendix 3.

This thesis is concluded by a discussion which draws together the findings of the experimental work and assesses how the work carried out has achieved the initial aims of the thesis. Future work is suggested which may aid in answering some of the questions which this thesis has raised.

Chapter 4.

Materials and methods

4. Materials and methods

The aims of the research described in this thesis were to improve the understanding of N₂O emissions from arable agricultural soils in Scotland and to investigate the potential for biochar to be used as an N₂O mitigation option. To achieve these aims, three field experiments and one laboratory experiment were undertaken. Numerous common materials and methods were used during these experiments, and this chapter describes the most important of these and the rationale behind their use. Further description of the methodologies used for individual experiments is available in Chapters 5, 6, 7 and 8. In addition to the work described in the aforementioned chapters, development of some of the methodologies used was carried out. The background to these methodological developments is described in this chapter, and further details are available in appendices 2 and 3. Tables 1 and 2 show the main materials and methods used in the work described in this thesis.

Chapter	Location	Materials used
5	Gilchriston farm	<ul style="list-style-type: none">• Soil• Fertilisers: Ammonium nitrate, urea• Nitrification inhibitor (Dicyandiamide, DCD)
6	Boghall farm	<ul style="list-style-type: none">• Soil• Fertilisers: Cattle slurry, layer manure, poultry litter• Nitrification inhibitor (Dicyandiamide, DCD)
7	SRUC Laboratory	<ul style="list-style-type: none">• Biochars: Miscanthus straw, oilseed rape straw, willow, softwood, hardwood• Ammonium nitrate solution
8	Boghall farm	<ul style="list-style-type: none">• Soil• Fertiliser: Cattle slurry (stored in tanks and spread on field)• Oilseed rape straw biochar

Table 1. *Table of experiment locations and materials used in each chapter.*

Variable measured	Method used	Chapter
N ₂ O flux	Static closed chamber method, analysis using gas chromatography <i>(Clayton, 1994; Jeffrey and Kipping, 1972)</i>	5, 6, 8
CO ₂ , CH ₄ flux	Static closed chamber method either on soil or slurry tanks, analysis using gas chromatography <i>(Clayton, 1994; Jeffrey and Kipping, 1972)</i>	8
Soil NH ₄ ⁺ -N and NO ₃ ⁻ -N	Sampling using soil auger, KCl extraction, colorimetric analysis <i>(Singh et al. 2011)</i>	5, 6, 8
Soil moisture	Sampling using soil auger, oven drying <i>(Robertson, 1999)</i>	5, 6, 8
Rainfall, air temperature, soil temperature, soil bulk density	Weather station, soil data loggers, soil cores <i>(Robertson, 1999)</i>	5, 6, 8
Crop yield	Hand collection, small plot harvester	5, 6, 8
Crop N content	C/N analyser	5, 6, 8
Fertiliser (or slurry) pH, NH ₄ ⁺ -N and NO ₃ ⁻ -N, uric acid, moisture	Laboratory analysis	6, 8
NH ₃ flux	Wind tunnel method and Skalar analysis <i>(Lockyer, 1984)</i>	6
Biochar pH	pH meter <i>(Angst et al. 2013)</i>	7
Biochar moisture	Oven drying <i>(Angst et al. 2013)</i>	7
pH, NH ₄ ⁺ -N and NO ₃ ⁻ -N content of ammonium nitrate and water solution	pH meter and colorimetric analysis <i>(Singh et al. 2011)</i>	7

Table 2. Table of methods used in each chapter.

4.1 Field experiment sites

Field experiments took place at two arable sites, Gilchriston farm and Boghall farm. The work described in Chapter 5 was carried out at Gilchriston and Chapters 6 and 8 were carried out at Boghall.

4.1.1 Gilchriston

Gilchriston is a commercial arable farm situated in East Lothian, Scotland, approximately 20 miles south east of Edinburgh (Grid reference: NT479658) (Figure 1). Gilchriston was selected as an appropriate location for an experiment to investigate the effect of synthetic N fertiliser applications on N_2O emissions from Scottish agricultural soil as it is in one of the principal geoclimatic zones which support agricultural production in the UK and was considered representative of agricultural conditions in Southern Scotland.



Figure 1. Map showing the location of Gilchriston farm. Location of field experiment outlined in yellow. (Google maps, 2014).

Gilchriston is located at an elevation of 165 m a.s.l and has a relatively dry climate, with a 30 year mean annual precipitation of 676 mm and a 30 year mean annual temperature of 8.65°C. Climatic conditions in the 12 months during which the experiment was carried out (April 2011-March 2012) were unusual with a dry spring receiving 70-90 % of the average long term rainfall, but an exceptionally wet summer receiving 170 % of the average long term rainfall (Figure 2). The soil in the field selected for the experiment is a sandy loam (Humbie series) with a mean pH value of 6.3, organic matter content of 4 % and mean bulk density value of 1.20 g cm⁻³. Prior to the experiment, the field in which the experimental plots were located had been subject to an arable rotation of spring barley, winter wheat and winter oilseed rape (2008-2010).

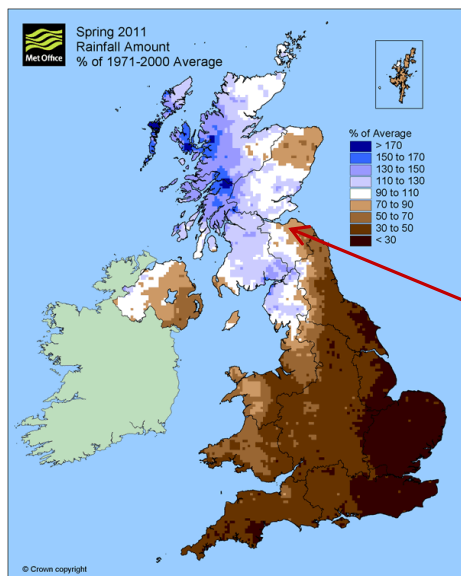


Figure 2a. Spring 2011 rainfall anomaly map for the UK (Met Office, 2014)

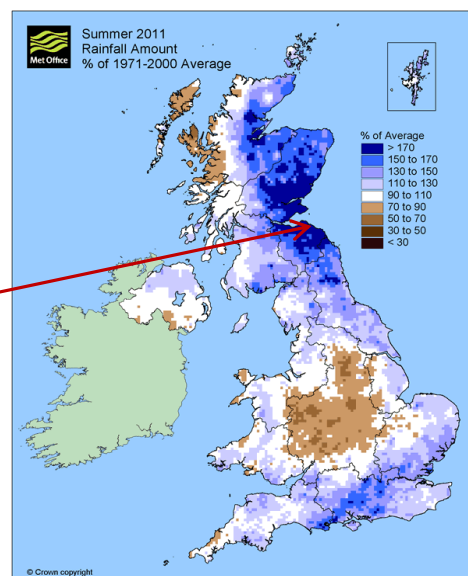


Figure 2b. Summer 2011 rainfall anomaly map for the UK (Met Office, 2014)

4.1.2 Boghall

Boghall is a commercial and research farm, situated on SRUC's Bush Estate, approximately 6 miles south of Edinburgh (grid reference NT 248654) (Figure 3). The estate has an area of 1013 ha, 74 ha of which is used for arable crops (SRUC, 2014). Following the experiment which was undertaken at Gilchriston farm in 2011-2012, it was not possible to apply organic fertilisers and biochar, and to continue working at Gilchriston, so a suitable replacement site was needed for the work described in chapters 6 and 8. Boghall was selected due to its location and similarities to the Gilchriston site. Boghall is located at an elevation of 190 m, has a 40 year (1955-1995) mean annual precipitation of 849 mm and mean daily temperatures in January and July of 3.8 °C and 13.3 °C respectively. Fertiliser applications for the work described in Chapter 6 took place in October 2012 and April 2013. Figure 4 demonstrates the differences between rainfall during the application periods in relation to the 30 year mean rainfall. During application in October 2012, 125-150 % of the average rainfall was received, in comparison to April 2013, during which time only 50-75 % of the average rainfall was received. The field in which the experiment was located has a sandy loam soil (Easter Bush/Darvel series). The soil has a mean pH of 6, organic matter content of 7 %, and bulk density value of 1.05 g cm⁻³. For the four years prior to our experiment taking place, the field in which it was located had a spring barley crop.



Figure 3. Map showing the location of Boghall farm. The location of the field experiment (chapters 6 and 8) is bordered in yellow and the orange circle shows the location of the barn in which the slurry tanks were stored during the work described in chapter 8 (Google Maps, 2014).

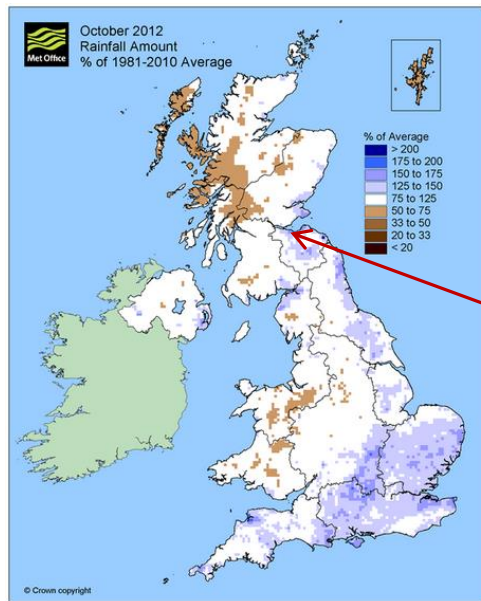


Figure 4a. *October 2012 rainfall anomaly map for the UK (Met Office, 2014)*

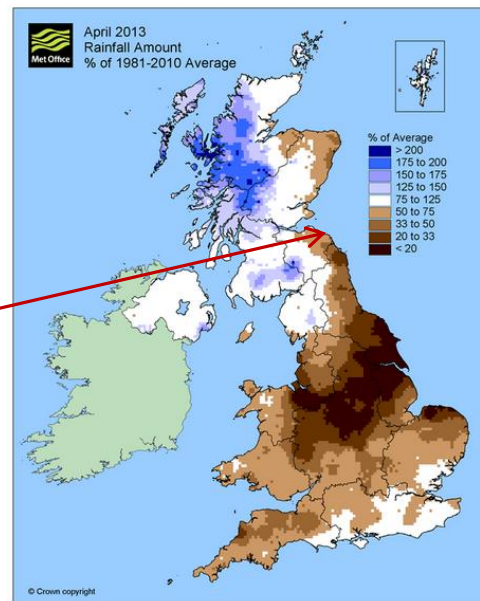


Figure 4b. *April 2013 rainfall anomaly map for the UK (Met Office, 2014)*

4.2 Summaries of main methods used

4.2.1 Static closed chamber methodology

The static closed chamber method was used in the work described in Chapters 5, 6 and 8 to measure N₂O, CO₂ and CH₄ fluxes from soil, in addition to the use of an adapted static closed chamber method to measure emissions of these gases from slurry stored in tanks in chapter 8. Using the static closed chamber method, the exchange of gas between the soil and the atmosphere is determined by measuring the increase in gas concentration in a known volume (the chamber) over a known period of time (Clayton, 1994). Static closed chambers which cover <1 m² of soil are a commonly used method to measure N₂O emissions from agricultural soils (Chadwick et al., 2014), primarily due to their ease of use, versatility and low cost (de Kleine et al., 2012). Static closed chambers are also suitable for measuring CH₄ fluxes from soils, however there can be issues when measuring CO₂ due to difficulties in differentiating soil and plant respiration, and uncertainties regarding the amount of photosynthesis occurring (Parkin and Venterea, 2010). Emissions of N₂O from soils have high spatial and temporal variability due to the heterogeneity of soil (Lilly et al., 2003) and the use of a large number of static closed chambers allows this variability to be taken into account. Chadwick et al. (2014) states that at present, the only means of measuring N₂O emissions from plot based field experiments which have replicated treatments and a blocked design (as do the experiments in Chapters 5, 6 and 8) is through the use of static closed chambers.

Static closed chamber methodologies and the design of chambers are highly variable, yet in order to achieve reliable results and to enable inter study comparisons of N₂O emissions it is necessary to use a common methodology (de Kleine et al., 2012). To this end, the global research alliance on GHGs (GRA) published nitrous oxide chamber methodology guidelines (de Kleine et al., 2012) to encourage the use of standard methodologies when using static closed chambers by determining the minimum requirements which must be taken into account. Issues which are considered in the GRA guidelines include chamber material, site disturbance, chamber deployment time, frequency of sampling and treatment replication. The chamber methodology used in Chapters 5, 6 and 8 meets the GRA criteria and is described in more detail in these chapters. The linearity of gas accumulation within a chamber is one of the key assumptions

underpinning static closed chamber methodology and is particularly important for methods such as the ones used in chapters 5, 6 and 8 where only one sample is taken from each chamber on each measurement occasion and time 0 (t_0) samples are taken as being the same as the ambient air, as linearity of gas accumulation within the chamber must be assumed. In theory, gas accumulation within a chamber is non linear due to a reduction in the concentration gradient between the soil and air as the accumulation of gas in the chamber increases, this leads to a decrease in the gas flux from the soil (Hutchison and Mosier, 1981). However, if chambers remain closed for only a short period of time (between 40-60 minutes) gas accumulation usually remains linear. Chadwick et al. (2014) tested this assumption by studying almost two thousand chamber measurements of N_2O taken using the methodology described in Chapter 5 and found that in 92 % of cases, N_2O concentration increase over a period of 40-60 minutes was linear. Figure 5 shows an example of linear increases in N_2O accumulation as measured at Gilchriston.

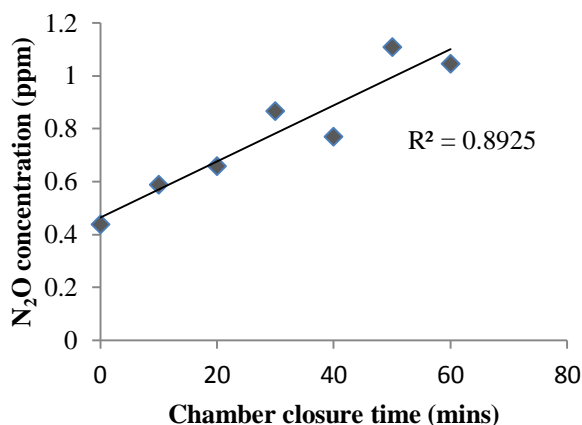


Figure 5. Linearity of N_2O accumulation in a static closed chamber (Gilchriston, 9th August 2011)

4.2.2 Determination of N_2O , CH_4 and CO_2 concentrations using gas chromatography

N_2O concentrations of the gas samples collected in pre-evacuated glass vials in the field were determined using gas chromatography. Gas chromatography separates and identifies the different components within a mixture (e.g. air samples) using a mobile and a stationary phase. Gas

chromatography involves the injection of the gas sample into a carrier gas which travels to a column on which the different components of the gas are separated due to variation in retention time of these components by the column. These components are then transported from the column by the carrier gas to the detector. The type of detector varies depending on the component of interest. For the work described in this thesis, the gas chromatograph used an Electron Capture Detector (ECD) to detect N_2O , a thermal conductivity detector (TCD) to detect CO_2 and a Flame Ionisation Detector (FID) to detect CH_4 (Jeffrey and Kipping, 1972). Three sets of certified calibration standards were analysed on the gas chromatograph each time unknown samples were analysed, these covered the range of expected concentrations of the unknown samples. The concentrations of the calibration standards were as follows: N_2O : 0.35, 1.1, 5.1, 10.7 ppm. CH_4 : 2, 5.2, 9.7, 22.1 ppm. CO_2 : 390, 1093, 5262, 10100 ppm. Daily N_2O , CO_2 or CH_4 fluxes were calculated using the equation described by Saggar et al. (2008). Cumulative fluxes were calculated as follows:

To find cumulative flux on day x (most recent sampling date) when previous sampling had been on day y:

$$= (\text{day x flux} + \text{day y flux}) + (\text{mean}(\text{day x flux} + \text{day y flux})) * (\text{day x date} - \text{day y date})$$

4.2.3 Determination of soil ammonium and nitrate concentrations using continuous flow analysis

Soil samples from 0-10 cm depth were collected frequently during the field experiments described in Chapters 5, 6 and 8. After sieving fresh soil to <4 mm and extraction by 2M KCl, extracts were analysed for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ content using a Skalar San⁺⁺ continuous flow autoanalyser. The following ranges of 2M KCl standards were used each time unknown samples were analysed: 0, 2, 4, 6, 8 and 10 mg/L $\text{NH}_4^+\text{-N}$ and 0, 1, 2, 3, 4 and 5 mg/L $\text{NO}_3^-\text{-N} + \text{NO}_2^-\text{-N}$. Determination of $\text{NH}_4^+\text{-N}$ is carried out at 660 nm and of $\text{NO}_3^-\text{-N}$ is carried out at 540 nm following the procedures described in Singh et al (2011).

4. 2.4 Measurement of ammonia emissions using wind tunnels

Ammonia (NH_3) emissions were measured during the work described in Chapter 6 using the wind tunnel method first used by Lockyer (1984). Further details of this method are given in Chapter 6. The use of wind tunnels is described as an enclosure technique for measuring NH_3 emissions. Such techniques are considered appropriate to use when measuring emissions from small plot based experiments, in contrast to micrometeorological methods which are generally used to measure emissions over a larger land area. The wind tunnel method is an example of an enclosure technique which uses open chambers (Misselbrook et al., 2005a). There are issues associated with the use of wind tunnels including decreased rainfall and increased temperature under the canopies, both of which may impact upon NH_3 emissions (Misselbrook et al., 2005a; Misselbrook et al., 2005b).

4.3 Development of methodologies

4.3.1 The effect of headspace mixing on N₂O emissions from static closed chambers

The static closed chamber method of measuring soil N₂O emissions relies on adequate mixing of the headspace air inside the chamber. However, current chamber design guidelines are vague when considering this issue and there has been a lack of research into the effects of headspace mixing on measured N₂O emissions from static closed chambers. As such, many researchers do not use chamber headspace mixing (de Kleine et al., 2012). Previous research on chamber headspace mixing has used fans to mix headspace air and measured CO₂ and CH₄ fluxes. It was found that fluxes were underestimated when headspace mixing did not take place (Christiansen et al., 2011; Rochette and Hutchinson, 2005). The chambers used in Chapters 5, 6 and 8 did not contain fans and the headspace air was unmixed. Therefore it was decided to carry out a controlled experiment in a glasshouse to investigate whether the use of small fans inside chambers to mix air affected N₂O flux measurements. This work is described further in Appendix 2.

4.3.2 Sterilisation of biochar by autoclaving

The batch sorption experiment described in chapter 7 required the use of sterile biochar, in order to be certain that any uptake of NH₄⁺-N and NO₃⁻-N was related to properties of the biochar and not due to the effects of microorganisms which may be present on the biochar. It was therefore decided to carry out a preliminary experiment to test whether autoclaving would be a suitable method of sterilising biochar. Further description of this experiment and the results obtained are available in Appendix 3.

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Chapter 5.

Managing fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities from a cultivated Cambisol in Scotland

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Managing fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities from a cultivated Cambisol in Scotland

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Abstract

Emissions of nitrous oxide (N_2O) were measured from an arable site in south east Scotland for twelve months during 2011- 2012 using an intensive sampling strategy. This fully replicated and blocked field experiment aimed to provide accurate measurements of N_2O emissions from one of the UK's principle geoclimatic zones supporting agricultural production and to produce robust N_2O emission factors (EFs). Calculated EFs were compared to the IPCC's default Tier 1 EF of 1.25 %, and the new value of 1 %, to assess their suitability for use in locations throughout the UK. Emissions from ten treatments fertilised with either ammonium nitrate or urea at rates of 0 kg N ha^{-1} to 200 kg N ha^{-1} , and sown with spring barley, were measured using the static closed chamber technique. Potential N_2O mitigation options were investigated; these included the use of a nitrification inhibitor (NI), split fertiliser applications and variations in the form and quantity of fertiliser applied. Crop yields were measured to enable calculation of N_2O emission intensities for each treatment; this is an important factor to consider when assessing N_2O mitigation options due to the need to maintain crop yields. Cumulative N_2O emissions varied between 1.32 $\text{kg N}_2\text{O-N ha}^{-1}$ and 3.82 $\text{kg N}_2\text{O-N ha}^{-1}$ with a mean 42 % decrease in emissions associated with the use of the NI. Increases in crop yield were associated with increases in N fertiliser application, and the amendment of treatments with a NI and the use of a split fertiliser application significantly decreased crop yields by approximately 10 % and 5 % respectively. Annual EFs ranged between -0.28 % to 1.35 %. Emission intensities decreased with increasing fertiliser application at low N application rates, and the optimum fertiliser application rate to obtain minimum emissions but maximum crop yield was 160 kg N ha^{-1} .

1. Introduction

Nitrous oxide (N_2O) is a powerful greenhouse gas (GHG) which accounts for 8 % of total global GHG emissions (Reay et al., 2012) and has a global warming potential 298 times greater than that of CO_2 (Forster et al., 2007). The breakdown of N_2O to NO in the stratosphere also results in the depletion of stratospheric ozone (Crutzen and Lelieveld, 2001). Although N_2O is a naturally occurring gas, there has been an increase in atmospheric concentration of 16 % since 1750 which is primarily attributed to emissions from fertilized agricultural soils (Davidson, 2009). Global annual emissions from agricultural soils are currently estimated to be around 4 Tg N_2O -N (Reay et al., 2012).

The production of N_2O by fertilised arable soils is associated with the application of inorganic N fertilisers and manures or soil disturbance, which cause an increase in soil concentrations of ammonium (NH_4^+) and nitrate (NO_3^-). These transformations are responsible for the subsequent production of N_2O as a byproduct of the microbial processes of nitrification and denitrification (Chapuis-Lardy et al., 2007; Inselbacher et al., 2011). Emissions from fertilised soils have high spatial and temporal variability (Flechard et al., 2007; Lilly et al., 2003) due to the influence of multiple factors such as soil water filled pore space (WFPS), soil compaction, pH and temperature on the N_2O source processes (Bessou et al., 2010; Castellano et al., 2010; Pierzynski et al., 2005; Smith et al., 2003). The high spatial and temporal variability of N_2O emissions from agricultural soils makes it difficult to accurately assess annual fluxes. It has been suggested that a solution to this problem is the use of high frequency long path length measurement techniques such as eddy covariance (Flechard et al., 2007). However, such methods require large areas and are typically of limited value in plot based field experiments where manipulation treatments are compared, and emission factors (EFs) need to be calculated (as an unfertilised control area is needed too). An alternative approach, used in this study, is the use of static chambers with high temporal and spatial replication (Chadwick et al., 2014). Previous studies of N_2O emissions from agricultural soils using the static closed chamber technique often involved the use of only a small number of replicate chambers per treatment and a low sampling frequency over a short period of time. For example, a number of studies have used six or less static chambers per treatment (Ball et al., 1999; Clayton et al., 1997; Dobbie et al., 1999; Dobbie and Smith, 2003; Smith et al., 2012). Previous studies have also often been

based on short measurement periods ranging from 5 days to 6 weeks after fertiliser application (Skiba and Ball, 2002; Skiba et al., 2002; Smith et al., 2012). Furthermore, previous studies have not always adequately captured temporal dynamics where gas samples were taken at intervals of 2-4 weeks (Rees et al., 2013).

The relationship between the amount of N fertiliser applied and the magnitude of N₂O emissions is quantified through the use of an EF (EF1) which expresses the quantity of N₂O-N emitted as a proportion of the N fertiliser applied. The EF calculation also accounts for background emissions which are largely due to mineralisation of crop residues (IPCC, 2006). Bouwman (1996) reviewed experiments of at least a year in length and recommended an EF (EF1) of 1.25 % of the N applied to express the relationship between applied N fertiliser and N₂O emissions. The IPCC subsequently used this as a “default EF” to enable calculation of countries’ N₂O emissions from soils receiving inorganic fertiliser N (IPCC, 1996). This value has since been revised downwards on the basis of more recent evidence to give an EF of 1 % of N applied for use in the Tier 1 methodology for calculating N₂O emissions (IPCC, 2006). However many countries including the UK have not yet adopted the 1 % EF in their national inventory calculations. This default EF attempts to estimate typical emissions across large spatial areas and time periods, however there is concern that local soil and climatic conditions, and the type and rate of fertiliser used can lead to significant variance from average conditions (Smith et al., 2012). The use of a 1.25 % EF has been controversial in Scotland where it has been demonstrated that large changes in soil WFPS may result in Scottish EFs which are atypical of the whole of the UK (Dobbie et al., 1999; Dobbie and Smith, 2003). This is reflected in calculated N₂O EFs ranging from 0.17 – 7 % for a range of N sources for Scottish agricultural soils (Clayton et al., 1997; Dobbie et al., 1999; Smith et al., 1998a). To improve the accuracy of agricultural N₂O reporting it is necessary for investigation into the effects of controlling variables on N₂O emissions and the appropriateness of utilising a 1.25 % EF, or the new 1 % EF, regardless of location, and this is particularly relevant in areas of the UK which may experience extreme or unusual climatic conditions.

Mitigation of agricultural N₂O emissions is necessary if we are to limit the contribution of agriculture to climate change. The use of nitrification inhibitors (NIs) such as dicyandiamide (DCD) which act to decrease N₂O emissions by deactivating the ammonia monooxygenase

enzyme used in the primary stage of nitrification (Amberger, 1989) have proved successful in mitigating agricultural N₂O emissions (Di and Cameron, 2003; Di et al., 2007) and have also demonstrated the potential to increase crop yields (Abalos et al., 2014). However, there has been little investigation into the effectiveness of DCD in UK agricultural systems and more research in this area is required. Another N₂O mitigation option which requires further investigation is the use of split applications of N fertiliser. Split applications result in the application of smaller individual doses of fertiliser, which reduces surplus N in the soil and decreases the potential for loss of N via transformation to N₂O or leaching, in addition to being more suitable for crop requirements (Burton et al., 2008), potentially increasing the nitrogen use efficiency of fertilisers. Reducing the amount of surplus N is an important method of decreasing N₂O emissions as it not only has positive impacts on the environment but is also financially beneficial for the farmer. Altering the amount or type of fertiliser applied is another means by which surplus N may be decreased, and research has indicated that the use of urea rather than ammonium nitrate (AN) fertiliser may result in lower N₂O emissions (Dobbie and Smith, 2003; Smith et al., 2012).

Although it is important to minimise N₂O emissions from agricultural soils, it will also be necessary in the future to produce greater quantities of food, meaning that crop yield must not be negatively impacted by mitigation options. Emission intensities i.e. the amount of N₂O produced per unit of crop yield, are therefore a vital indicator of the potential of any N₂O mitigation option (Van Groenigen et al., 2010), although research into this area has thus far been limited.

This work forms part of a nationwide project to assess the effect of a range of organic and inorganic nitrogen fertiliser treatments on N₂O emissions from agricultural soils with the results being used to improve agricultural management systems and to reduce uncertainty in the UK agricultural greenhouse gas inventory (GHG, 2013). More specifically, the aims are to:

- i). Compare N₂O emissions, calculated EFs and emission intensities from different inorganic fertiliser treatments
- ii). Investigate the efficacy of potential N₂O mitigation options.
- iii). Assess the appropriateness of the use of the standard 1.25 % or 1 % EF for the area under investigation.

2. Materials and Methods

2.1 Site description

The experiment began in April 2011 at Gilchriston in south east Scotland (Grid reference: NT479658). Gilchriston is a commercial arable farm, selected for its location in one of the principal geoclimatic zones which support arable production in the UK. The site characteristics are described in Table 1. Soil pH, organic matter and bulk density were calculated using field measurements, other soil information was obtained from Hipkin (1989).

Table 1. *Gilchriston site characteristics.*

Site characteristic	Description
Elevation	165m
30 year mean precipitation	676 mm
30 year mean air temperature	9°C
Total precipitation (April 2011-April 2012)	822 mm
Mean air temperature (April 2011- April 2012)	9°C
Soil texture	Sandy loam
Soil series	Humbie
Soil group	Cambisol
Soil parent material	Reddish brown clay loam till
Soil drainage class	Imperfect
Soil structure	Moderate medium blocky
Soil stone content	Slightly stony
Soil pH	6.3
Soil organic matter	4%
Average soil bulk density	1.20 g cm ⁻³
Gravimetric water content at field capacity	21%
Crop type	Spring barley (<i>Hordeum vulgare</i> cv. Optic)
Sowing date	22 nd March 2011
Sowing rate	360 m ⁻²
Harvest date	22 nd August 2011
Crop 2010	Spring barley
Crop 2009	Winter wheat
Crop 2008	Winter oilseed rape

2.2 Experimental design

Nitrogen fertiliser treatments were compared that ranged from a control (0 kg N ha⁻¹) to 200 kg N ha⁻¹ and included the recommended application rate for the area of 120 kg N ha⁻¹ (Defra, 2010). The fertiliser was applied either in the form of ammonium nitrate (AN) or urea. Fertiliser

was applied in two doses (three doses for one treatment) in April and May 2011, by hand to the entire plot, to simulate agronomic practice. The NI DCD was applied at a rate of 10 kg ha⁻¹ as a spray an hour after the application of AN and urea. Further details of treatments are presented in Table 2. The experimental layout consisted of 10 m x 3 m plots replicated three times for each treatment in a randomized block design. For the duration of the experiment, pesticides were applied according to standard recommendations, and P₂O₅ and K₂O were applied to all plots at rates of 60 kg ha⁻¹ and 90 kg ha⁻¹, respectively, in order to satisfy crop demand.

Table 2. Treatment application rates and annual cumulative N_2O emissions and annual, seasonal and 5-week emission factors (EFs)

Treatment	Total application Rate (kg N ha ⁻¹) ^a	N	Annual mean cumulative N_2O (kg N_2O -N ha ⁻¹)	Annual mean cumulative N_2O Standard Error	Annual N_2O EF (% of N applied)	Annual EF Standard Error	Seasonal N_2O EF (% of N applied)	Seasonal EF Standard Error	5 week N_2O EF (% of N applied)	5 week EF Standard Error
Control	0		1.66	0.41	-	-	-	-	-	-
AN 40	40		2.02	0.53	0.90	2.33	0.39	1.36	0.44	0.08
AN 80	80		1.82	0.12	0.20	0.62	0.18	0.40	0.49	0.20
AN 120	120		3.28	0.12	1.35	0.31	0.45	0.23	0.54	0.17
AN 160	160		3.20	0.44	0.96	0.10	0.75	0.21	0.56	0.20
AN 200	200		3.82	0.11	1.08	0.26	0.86	0.28	0.46	0.08
AN 120 + NI	120		2.05	0.61	0.33	0.40	0.00	0.12	0.34	0.10
Urea 120	120		2.42	0.70	0.64	0.44	0.43	0.21	0.51	0.15
Urea 120 + NI	120		1.32	0.70	-0.28	0.63	-0.04	0.31	0.15	0.04
AN 120 (3 splits) ^b	120		2.93	0.28	1.06	0.25	0.57	0.35	0.50	0.16

^a Fertiliser was applied on 8th April and 26th April 2011

^b Additional split treatment was applied on 4th May

2.3 Gas and soil sampling, measurements and analysis

Nitrous oxide fluxes were measured at the experimental site over a one year period (7th April 2011 – 30th March 2012) using the static closed chamber technique (Chadwick et al., 2014; Clayton et al., 1994) and with a methodology that was consistent with Global Research Alliance guidelines (de Kleine and Harvey, 2012). Although the N₂O results are referred to as “annual” emissions, the precise number of days this period represents is 358 days. The intense N₂O sampling frequency was based on the assumption that most of the total direct N₂O emissions occur within the first month following each dose of fertiliser application (Dobbie et al., 1999). The sampling strategy therefore involved around 50 % of the total N₂O measurements occurring during this period of expected high emissions in order to capture the variations between treatments.

Five circular chambers made of opaque polypropylene (200 mm diameter, 300 mm height and soil surface area coverage of approximately 0.126 m²) were installed per plot, resulting in the use of 15 chambers per treatment. Chambers were installed by cutting a 5 cm deep slot into the soil and inserting the base of the chamber into this slot. Soil was tightly packed around the base of the chamber (on the outside) to ensure a good seal. The chambers were left in place for the whole experiment except when agricultural operations such as harvest deemed removal necessary. Extensions were added to the tops of the chambers during the growing season in order to avoid damaging the plants within the chambers. On each sampling occasion, aluminium lids were clipped onto the top of each chamber and the chamber remained covered for 40 minutes. The headspace was then sampled through a small sampling port in the lid using a syringe and gas samples were transferred to pre-evacuated 20-22 ml glass vials. Ambient and ‘linearity check’ gas samples were also collected. The linearity check involved collecting samples at 10 minute intervals from 3 randomly selected chambers (1 from each block) throughout the sampling period. Sampling was conducted between 10:00 and 12:00 h to ensure consistency. See Chadwick et al. (2014) for further methodology information.

Gas samples were analysed for N₂O concentrations using an Agilent 7890A Gas Chromatograph (GC) fitted with an electron capture detector (Agilent Technologies, Berkshire, UK) and a CTC Analytics COMBI PAL autosampler (CTC Analytics, Hampshire, UK). The GC response was calibrated using certified N₂O gas standards (0.35, 1.1, 5.1, 10.7 ppm) and the N₂O limit of detection was 0.025ppm. Air temperature was recorded on every N₂O sampling occasion and chamber height was also measured for use in N₂O flux calculations. Daily N₂O fluxes were calculated using linear regression which assumes a linear increase in N₂O concentration in a known volume over a known period of time, and the ideal gas law (Saggar et al., 2008). Cumulative N₂O fluxes from each chamber were calculated using the trapezoidal rule (area under the curve) to interpolate fluxes between sampling points. For each treatment, cumulative fluxes were calculated using the mean of the 5 chambers per plot, in order to calculate a treatment mean cumulative emission value and associated standard error.

Composite soil samples consisting of five cores (0-10 cm depth) collected at random locations using a 30 mm diameter auger were taken from each block on each N₂O sampling occasion for soil gravimetric water content (GWC) determination, i.e. one soil moisture content measurement per block on each occasion. Composite soil samples from each plot were also collected in this way at approximately monthly intervals throughout the one-year experiment for soil mineral N content determination, i.e. generating one sample per plot. Fresh soil samples were sieved (<4mm) and extracted using 2M KCl (soil to extractant ratio 1:2) for determination of soil ammonium (NH₄⁺-N) and nitrate (NO₃⁻-N) contents using a Skalar San⁺⁺ continuous flow autoanalyser (Skalar, York, UK). Soil bulk density was determined for each block through collection of intact soil samples using metal rings on frequent occasions throughout the experiment. Soil bulk density and GWC were used to calculate soil WFPS (%) on each gas sampling occasion (Robertson, 1999).

A meteorological station at the site recorded daily rainfall. Air and 10-cm depth soil temperatures were also recorded using a temperature probe (RS Components, Northamptonshire, UK) on each N₂O sampling occasion.

The crop was harvested on 22nd August 2011 using a small plot harvester which harvested an area of 15m² from each plot. Just prior to harvest, a random sample of 100 tillers per plot was also collected by hand. This was threshed and weighed to determine the ratio of grain to straw and chaff. The % dry matter and N content of the grain, and the mixed straw and chaff, from each plot was determined.

2.4 Emission Factor calculation

Emission factors, which express the N₂O-N emitted from each treatment as a percentage of the total N applied, were calculated (subtracting control values from each of the 3 blocks from corresponding treatment values as appropriate before calculating mean treatment EFs) using the following equation:

$$EF = \left(\frac{\text{Cumulative annual } N_2O \text{ flux (kg } N_2O\text{-N)} - \text{cumulative annual } N_2O \text{ flux from control (kg } N_2O\text{-N)}}{N \text{ applied (kgN)}} \right) \times 100$$

Although 10 % of applied synthetic N fertiliser is thought to be emitted as NH₃ (IPCC, 2006), the N₂O EF described above does not take this into account. N₂O emissions are calculated based on the amount of N fertiliser applied and it is standard practice to calculate losses of N via other pathways i.e. by NH₃ volatilization or N leaching, using separate emission factors, however due to resource constraints this was not included in this work. EFs were calculated for three separate timescales: 1). An annual EF was calculated as recommended by Bouwman (1996). 2). A “seasonal” EF was calculated which included N₂O data up until harvest to take into account the effects of crop growth on N₂O emissions and the time taken for soil mineral N levels to return to “background” levels. 3). A “five week” EF was calculated for the 5 weeks following the first fertiliser application. This time scale was chosen as it has been reported that the majority of emissions take place during the 4 weeks following fertiliser application

(Dobbie et al., 1999) and would therefore enable clearer identification of treatment effects. However, due to dry weather during this period there were very low N₂O emissions from all treatments, so it was extended to 5 weeks to include the large peak in emissions which occurred during May.

2.5 Statistical analysis

Statistical data analyses were carried out using Genstat (16.1). The occurrence of any significant differences in measurements between treatments was tested using one-way analysis of variance (ANOVA) with blocks. Data were checked for normality before ANOVAs were applied and analysis of residuals was used to determine outliers. Two outliers were identified during the analysis of the cumulative N₂O data and the annual and seasonal EFs, these were from blocks 2 and 3 of the AN 40 treatment. These outliers were subsequently excluded from the analysis. Treatment effects were deemed significant if $p \leq 0.05$. Regression analysis was performed to determine the relationship between nitrogen applied and the cumulative annual emission. The REML procedure was used for this analysis with nitrogen level, specified as a variate, as the fixed factor, and the block was specified as the random factor. REML regression was also used to analyse the relationship between the daily N₂O emissions and the % WFPS with the block specified as the random factor. In this case, the emissions were transformed using natural logarithms. Due to large negative emissions, 25 g N₂O-N ha⁻¹ d⁻¹ was added to the emissions before transformation. On analysis of the residual plots, one outlier was identified and removed from the analysis (Block 2 on 7th July).

3. Results

3.1 Nitrous oxide fluxes

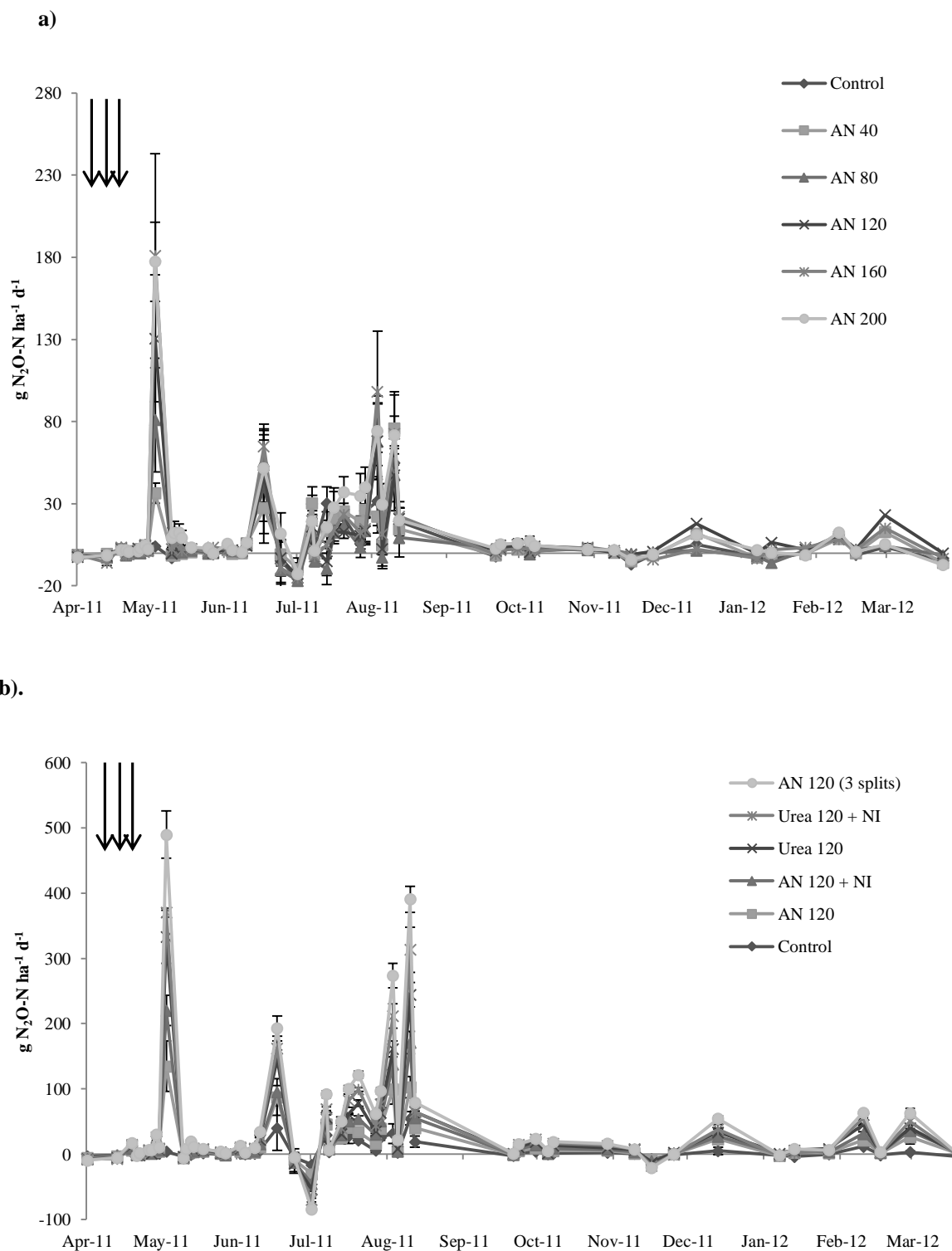
Nitrous oxide fluxes showed high temporal variation with most emissions occurring during a few intermittent flux episodes, and also varied widely between treatments (Figure 1). Emission maxima of 170-190 g N₂O-N ha⁻¹ d⁻¹ from the AN 160 and AN 200 treatments occurred 13 days after the second fertiliser application in May 2011. Total N₂O emissions were higher in August than any other month with a maximum cumulative monthly value of 0.013 kg N₂O ha⁻¹ from the CON treatment. Negative N₂O fluxes were occasionally observed during the experimental period with the largest negative flux of -18 g N₂O-N ha⁻¹ d⁻¹ occurring for the AN 80 and urea 120 + NI treatments in July.

Cumulative N₂O emissions for the one year study period showed marked treatment effects (Figure 2), with a general increase in cumulative N₂O emissions associated with larger N applications. During the 1 way ANOVA with blocks, 2 outliers were observed from the analysis of the residuals. These were the cumulative emissions from blocks 2 and 3 of the AN 40 treatment and these were subsequently removed from the analysis. Maximum cumulative emissions were recorded from the AN 200 treatment with a value of 3.82 kg N₂O ha⁻¹. Cumulative emissions from the AN 200 treatment were significantly higher ($p=0.009$, SED = 0.605) than from the CON, urea 120, urea 120 + NI, AN 120 + NI, AN 40 and AN 80 treatments. The lowest cumulative N₂O emissions were from the Urea 120 + NI treatment with a value of 1.32 kg N₂O ha⁻¹. This was a non significant 45 % reduction in cumulative emissions in comparison to the urea 120 treatment. There was a significant 38 % decrease in cumulative emissions from the AN 120 + NI treatment in comparison to the AN 120 treatment; however there was no significant difference between the AN 120 + NI and that AN (3 splits). Cumulative N₂O emissions from the AN (3 splits) and urea 120 treatments showed a trend for lower emissions than from the AN 120 treatment by 11 % and 26 %.

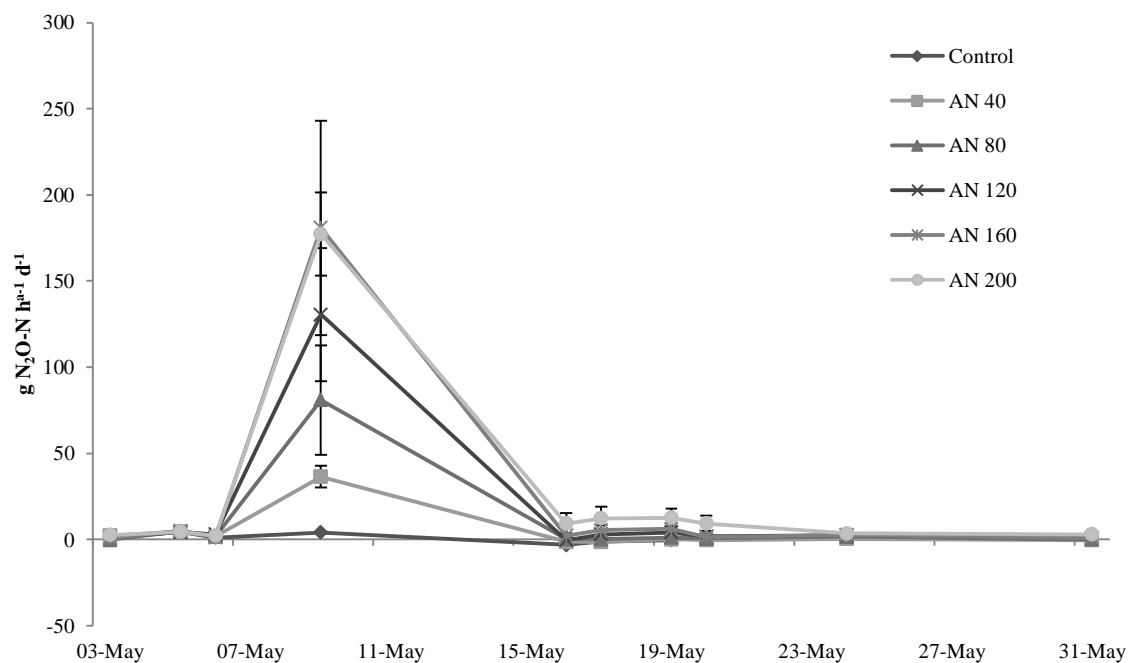
3.2 Environmental conditions

The weather during the experimental period was atypical for this region, with a dry spring, followed by an unusually wet summer which coincided with low temperatures (Figure 3a and b). The high N₂O emissions observed during the summer corresponded with the occurrence of most of the large rainfall events during this period (Figures 1 and 3). The May emission peak occurred in a relatively dry period (the soil WFPS was 38 %) but during the peak in emissions in August the soil was considerably wetter (soil WFPS values of ~50 %). Despite the high rainfall, only 4 % of the measurement days had 50-70 % WFPS with all of the remaining days having < 50 % WFPS. A WFPS value of >60-70 % is generally associated with denitrification conditions, and hence with greater N₂O fluxes (Davidson, 1991).

Figure 1. *a).* AN fertiliser dose response: N_2O emissions during the experimental period. *b).* Mitigation options and comparable treatments: N_2O emissions during the experimental period. *c).* AN fertiliser dose response: N_2O emissions during the May emission peak. *d).* Mitigation options and comparable treatments: N_2O emissions during the May emission peak. On all graphs: ($N=3$; error bars are \pm one standard error). Arrows indicate the timing of fertiliser applications.



c).



d).

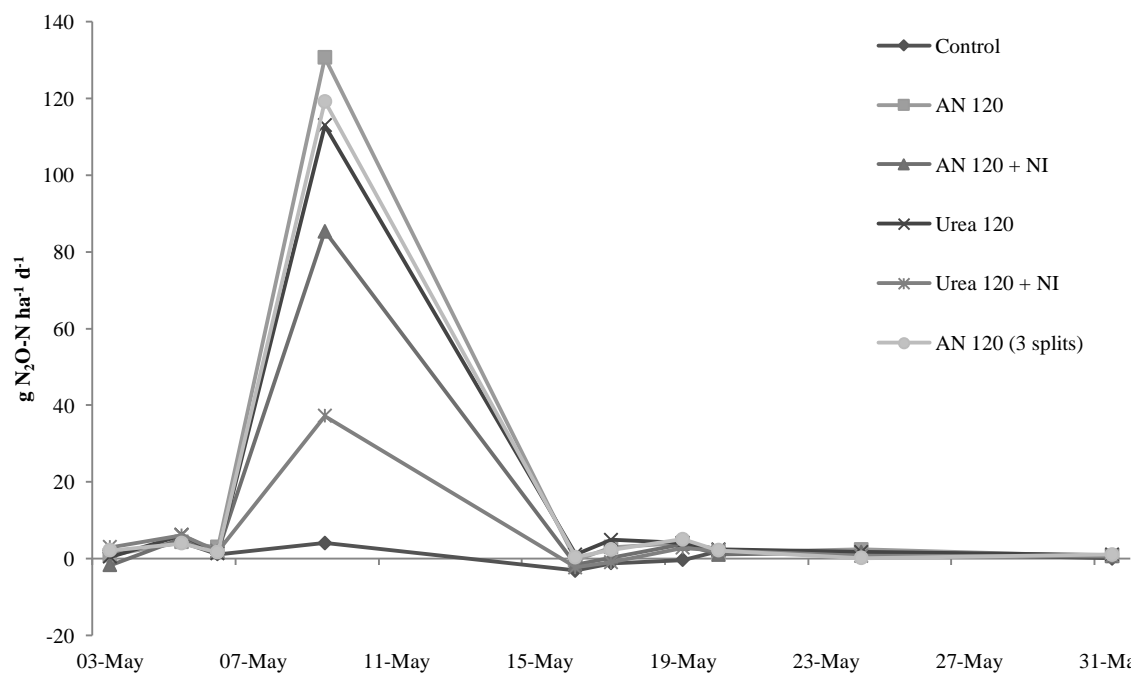
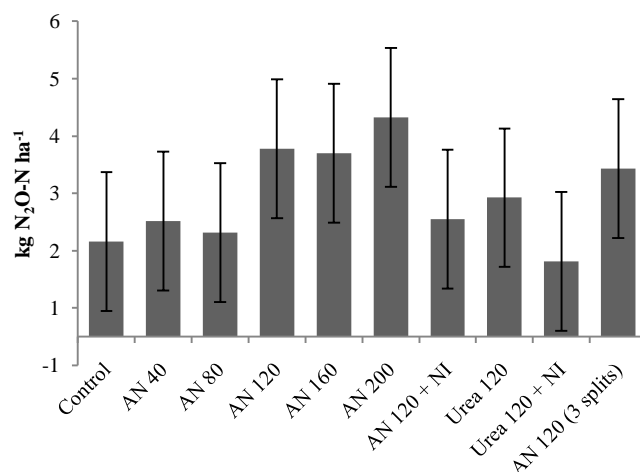


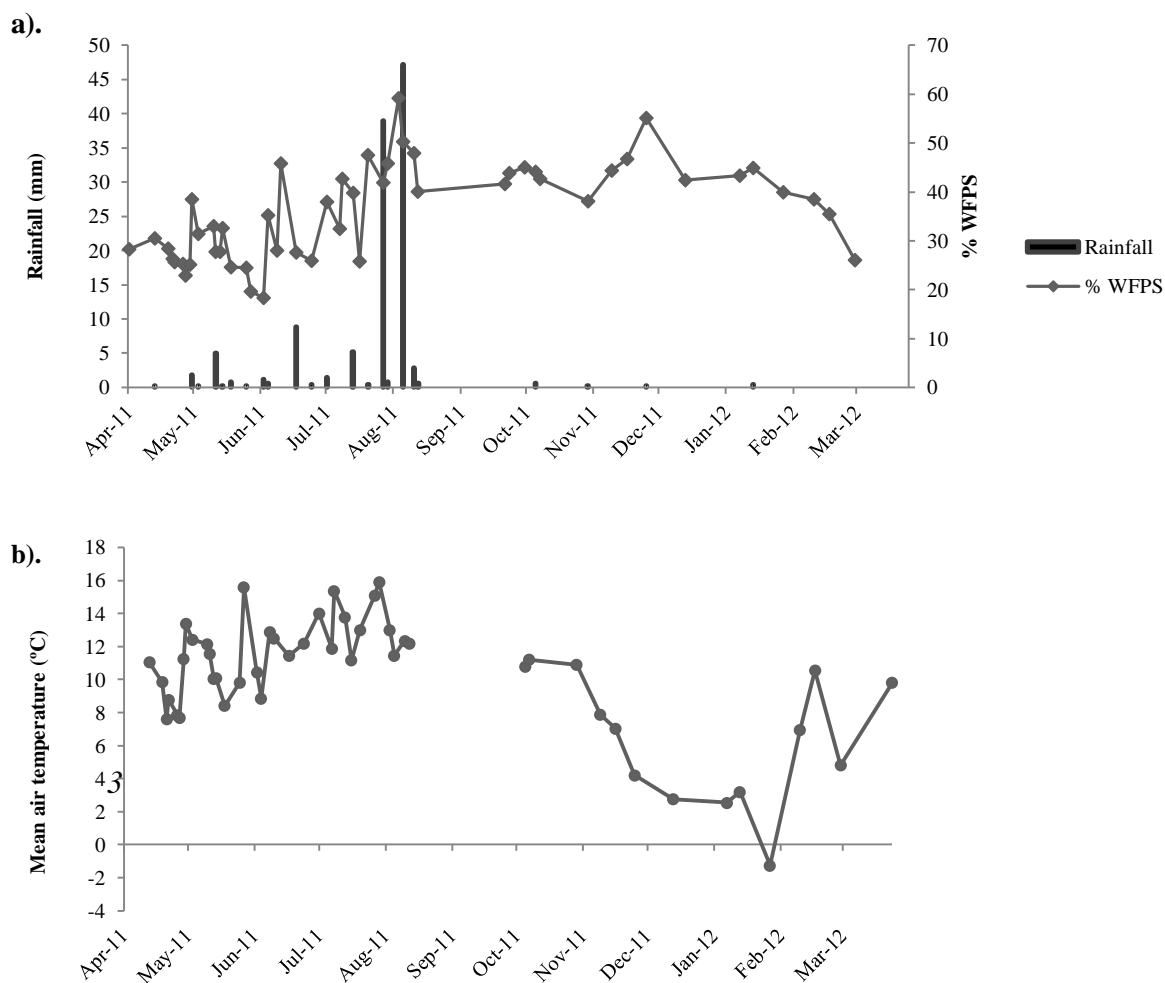
Figure 2. Mean annual cumulative N_2O emissions for each treatment ($N=3$; error bars are l.s.d = 1.21)



3.3 Emission factors

Emission factors for each time period (annual, seasonal and 5 weeks) were calculated (Table 2). The maximum annual EF was 1.35 from the AN 120 treatment and the mean annual EF was 0.69, in comparison to the mean seasonal EF of 0.40 and the mean 5 week EF of 0.44. Two negative EFs were obtained for the annual and seasonal urea 120 + NI treatment. These represent positive emissions which are lower than the unfertilised control due to the EF calculation method used, in which control fluxes are subtracted from treatment fluxes. There were no significant differences between EFs for all treatments at any of the three timescales (EF annual, $p=0.082$; EF seasonal, $p=0.082$; EF 5 wk, $p=0.209$).

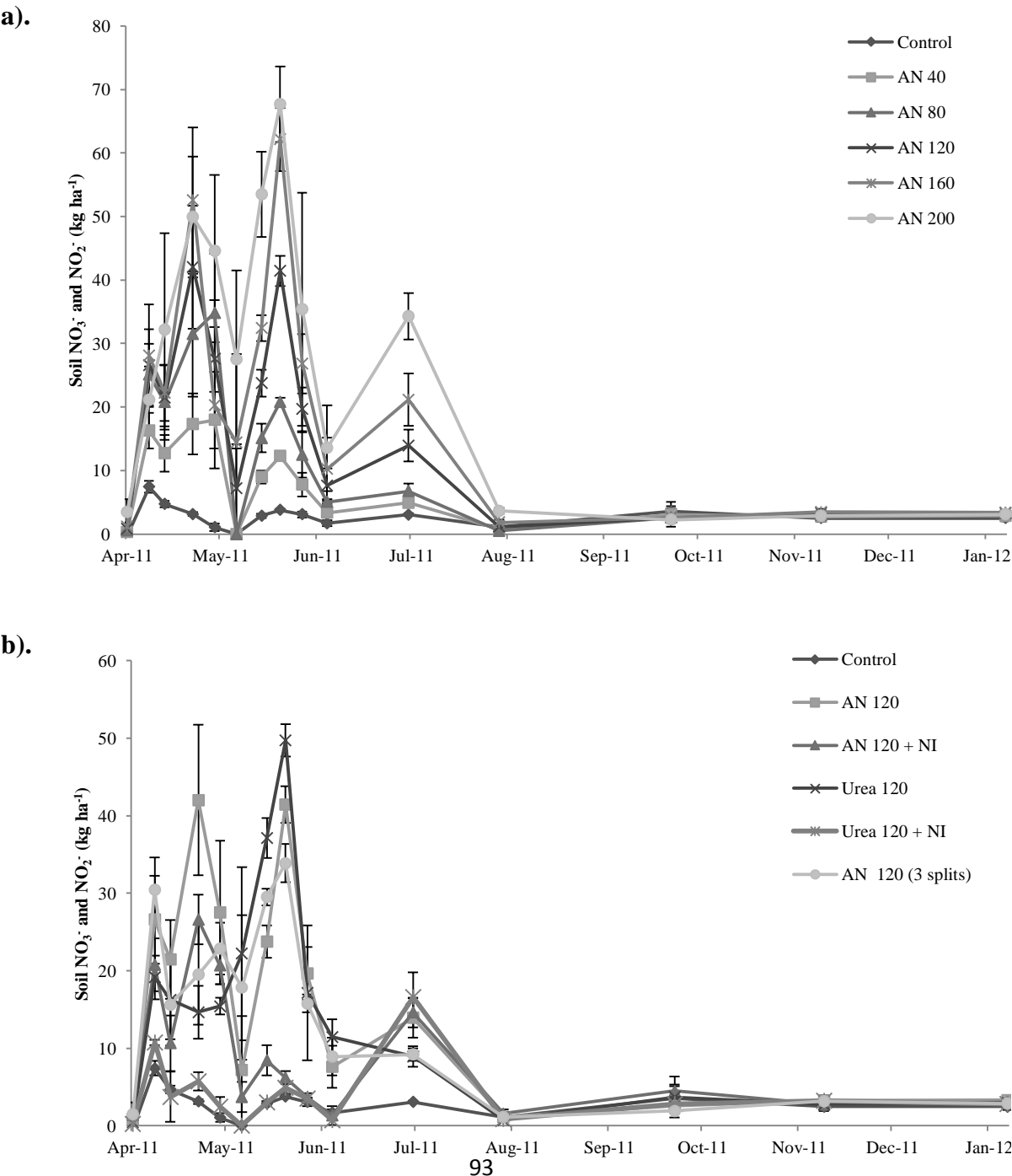
Figure 3. a). %WFPS and daily rainfall during the measurement period. b). Mean air temperature on sampling days during the measurement period.



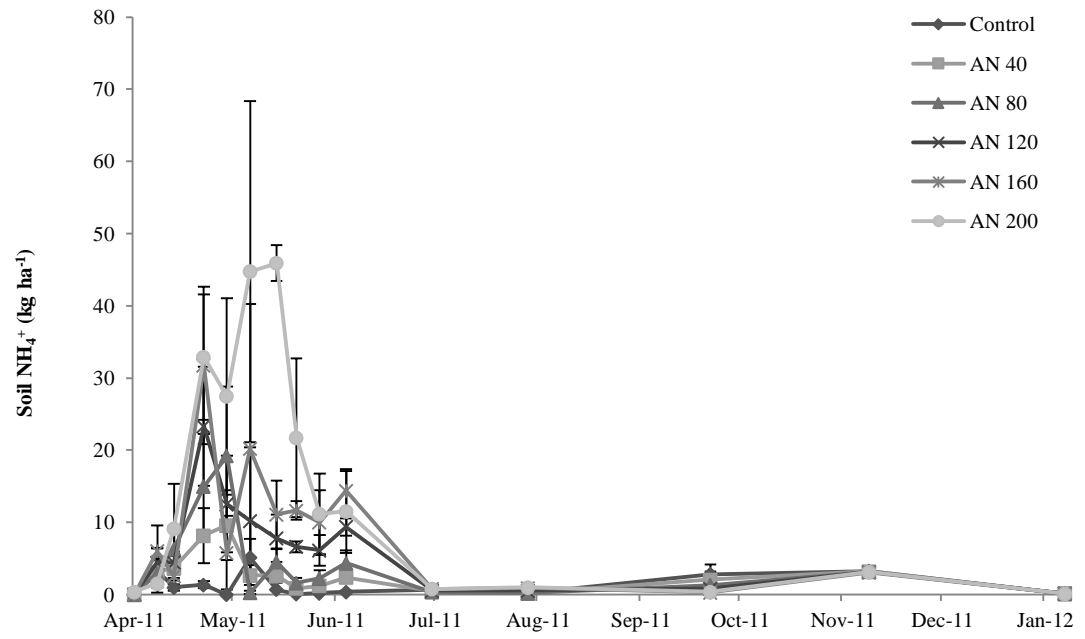
Soil NO_3^- -N and NH_4^+ -N concentrations increased following fertiliser application with a peak in NO_3^- -N concentration of 68 kg N ha^{-1} in the AN 200 treatment and a peak in NH_4^+ -N concentration of 57 kg N ha^{-1} in the urea 120 + NI treatment, just over a month after the final fertiliser application (Figure 4). As expected the mineral N concentrations increased as the application rate of AN fertiliser increased. The NI treatments acted to significantly increase NH_4^+ -N concentrations ($p < 0.05$) and significantly decrease NO_3^- -N concentrations ($p < 0.05$) in comparison to the non-NI amended treatments. Following peak soil NO_3^- -N and NH_4^+ -N concentrations, values decreased to $< 5 \text{ kg N ha}^{-1}$. The

concentrations of both NO_3^- -N and NH_4^+ -N were consistently below 5 kg N ha^{-1} in the period between August 2011-March 2012.

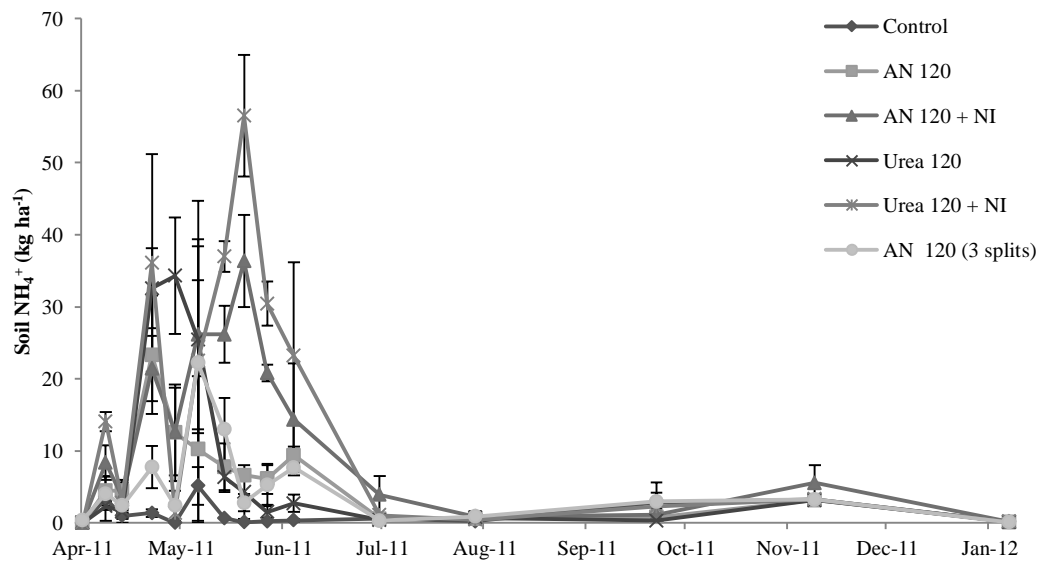
Figure 4. Soil mineral N contents during the experimental period at Gilchriston **a).** AN fertiliser dose response: Soil $\text{NO}_3^- + \text{NO}_2^-$ contents. **b).** Mitigation options and comparable treatments: Soil $\text{NO}_3^- + \text{NO}_2^-$ contents. **c).** AN fertiliser dose response: Soil NH_4^+ contents. **d).** Mitigation options and comparable treatments: Soil NH_4^+ contents. ($N=3$; error bars are \pm one standard error)



c).



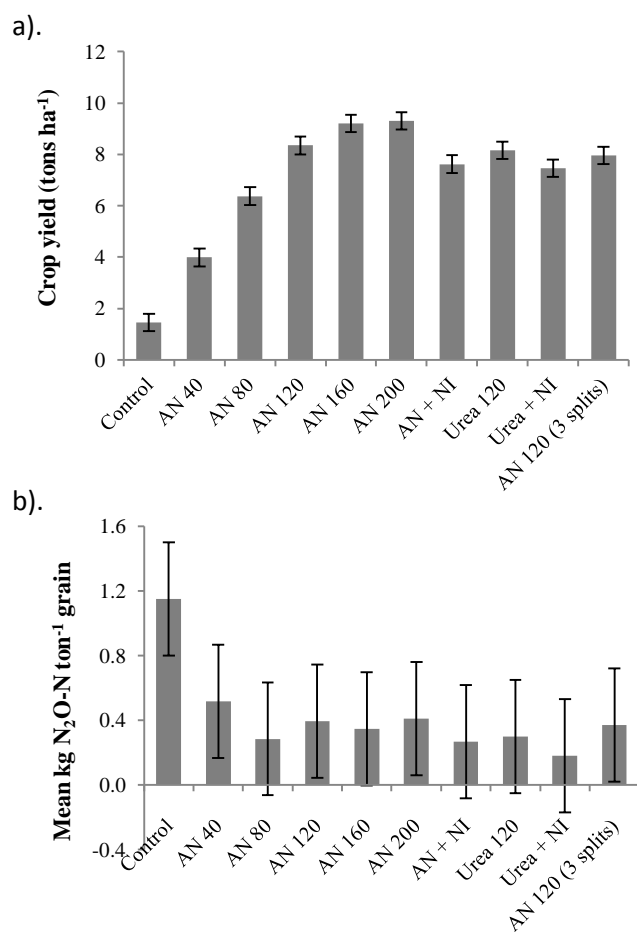
d).



3.5 Crop yield and yield scaled emissions

Crop yield (grain harvest at 15 % dry matter) ranged from a minimum of 1.46 t ha⁻¹ for the control treatment to 9.30 t ha⁻¹ for the AN 200 treatment (Figure 5a). Significantly greater crop yield was obtained from the AN 160 and AN 200 treatments ($p < 0.001$, SED = 0.1682) than from all other treatments. The crop yield obtained was dependent on the amount of N fertiliser applied, with greater crop yield obtained for larger applications of N fertiliser. Crop yield was significantly decreased by 9 % and 10 %, respectively for the AN 120 + NI and the urea 120 + NI treatments in comparison to their non NI amended counterparts and there was significantly lower crop yield from the AN (3 splits) treatment in comparison to the AN 120 treatment. Yield scaled emissions generally decreased with increasing rates of N fertiliser application from a maximum of 1.15 kg N₂O ton⁻¹ grain for the control treatment, to a minimum of 0.18 kg N₂O ton⁻¹ grain for the urea 120 + NI treatment (Figure 5b). There was a significant effect of treatment on yield scaled emissions ($p = 0.002$, SED = 0.1742) which showed that the control treatment had significantly higher emission intensities than the fertiliser treatments.

Figure 5. a). 2011 harvest grain yield for each treatment. ($N=3$; error bars are $l.s.d= 0.34$. b). N_2O intensity of grain yield ($kg\ N_2O-N$ per ton of grain) ($N=3$; error bars are $l.s.d= 0.35$)

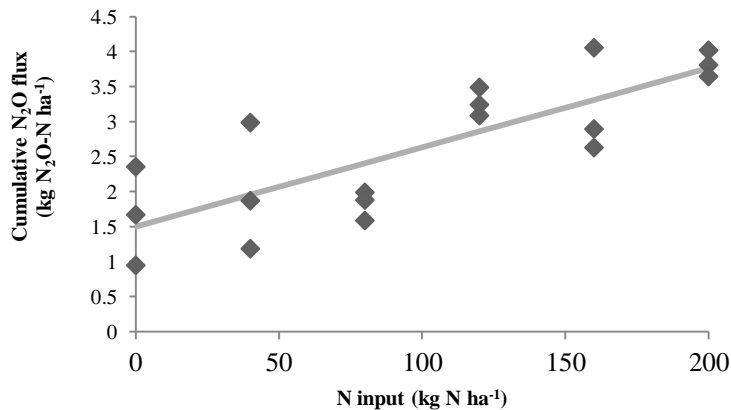


4. Discussion

4.1 Linearity of N₂O emissions with N application

This study demonstrated the value of a high intensity sampling strategy in assessing variability in N₂O emissions between fertiliser treatments. Greater applications of N fertiliser generally resulted in higher cumulative N₂O emissions due to the increase in soil NO₃⁻ and NH₄⁺ contents. There was a strong linear relationship ($p < 0.001$) between the amount of N fertiliser applied and the magnitude of the cumulative N₂O emissions (Figure 6). Treatments AN 80 and AN 120 demonstrated smaller variability in N₂O emissions between blocks in comparison to the other treatments. The IPCC Tier 1 EF approach assumes that N₂O emissions are a linear function of N application (Philibert et al., 2012) and our results support this assumption, in contrast to some suggestions that the relationship between N input and N₂O emissions may be non-linear (Hoben et al., 2011; McSwiney and Robertson, 2005).

Figure 6. Linear relationship between N input (0-200 kg AN ha⁻¹) and cumulative N₂O fluxes from each block. $Y = 0.01131 (\pm 0.002067) x + 1.501 (\pm 0.2503)$. $p = < 0.001$ $r^2 = 0.86$



4.2 Cumulative N₂O emissions and environmental controls

Cumulative annual emissions from all treatments were particularly high in comparison to comparable experiments in this area. McTaggart et al. (1997) and Smith et al. (1998a) measured N₂O emissions from spring barley crops fertilised with 120 kg N ha⁻¹ in South East Scotland in 1993 and 1994-1995 respectively and reported emissions of 0.8 kg N₂O-N ha⁻¹, considerably lower than the 3.28 kg N₂O-N ha⁻¹ reported for the AN 120 treatment from our experiment. The lower frequency of measurements carried out by McTaggart et al. (1997) and Smith et al. (1998a) may explain their reported lower emissions. The high emissions observed during this experiment contrasts with work by Smith et al. (1998a), which reported that emissions from Scottish sites were generally small due to low spring and summer temperatures which reduces the production of N₂O. Most of the N₂O emissions are expected to occur in the four weeks following fertiliser application (Bouwman, 1996) and the mean soil temperature recorded during this period for our experiment was 13.3 °C, only 0.6 °C lower than the maximum mean monthly soil temperature observed in July which will have promoted high N₂O production.

Previous work by Dobbie et al. (1999), Flechard et al. (2007), Jones (2007) and Rees et al. (2013) has demonstrated that the key factors affecting N₂O emissions from N fertilised agricultural soils are % soil WFPS, soil temperature and soil mineral N. However, there are threshold levels of these factors and if this threshold is not exceeded by any of these variables then N₂O production may be limited (Dobbie and Smith, 2003; Topp et al., 2013). During the period immediately following fertiliser application and the subsequent summer months when soil mineral N contents and temperature were not limiting to N₂O production, the primary variable affecting emissions was % soil WFPS. This limiting effect was clearly demonstrated in this experiment in the period between the first fertiliser application and the large peak in emissions approximately four weeks later. During this period the mean soil temperature of 13°C would not have been limiting to N₂O production, however, low % soil WFPS would have been (Figures 1 and 3). A large rainfall event in early May (Figure 3) increased % soil WFPS from a mean value of 27 % to 39 % which increased N₂O emissions (Figures 1 and 3). During the peaks in

N₂O emissions in August, % soil WFPS values were approximately 46 % (Figures 1 and 3), however, at this time soil mineral N had returned to below what is considered a threshold level of 5 mg N kg⁻¹ (5.95 kg N ha⁻¹), which implies that soil WFPS has greater control over the potential for N₂O production than soil mineral N contents. The relationship between flux response and % soil WFPS was analysed for the highest N fertiliser treatment for this experiment. When N₂O data from the one year measurement period is used, including periods in which soil NO₃⁻ is below 5 mg N kg⁻¹, there is a significant positive relationship between N₂O and soil WFPS (p<0.001) (Figure 7a). When periods in which soil NO₃⁻ <5 mg N kg⁻¹ are removed (Figure 7) there is also a significant positive relationship between N₂O and soil WFPS (p<0.001) (Figure 7b), in agreement with Dobbie et al. (1999) who also found a significant relationship (p<0.05) when the same limitations were applied.

The observation of a significant relationship between N₂O emissions and % soil WFPS, even when soil NO₃⁻ was < 5mg N kg⁻¹ is in contrast to previous studies of Scottish arable sites which found no relationship between these variables below an NO₃⁻ threshold of 5mg N kg⁻¹ (Clayton et al., 1997; Dobbie et al., 1999; Smith et al., 1998a). The relationship between N₂O flux and % soil WFPS is related to the dominance of either nitrification or denitrification as the N₂O producing processes. Davidson (1991) suggested that denitrification predominates at soil WFPS >60 % and that at values <60 %, nitrification is the dominant process. In this study, despite greater than average annual rainfall, the 60 % WFPS threshold was never exceeded. This combined with the return of NH₄⁺ concentrations to background levels prior to the NO₃⁻ concentrations suggests that nitrification may have been the dominant N₂O production process.

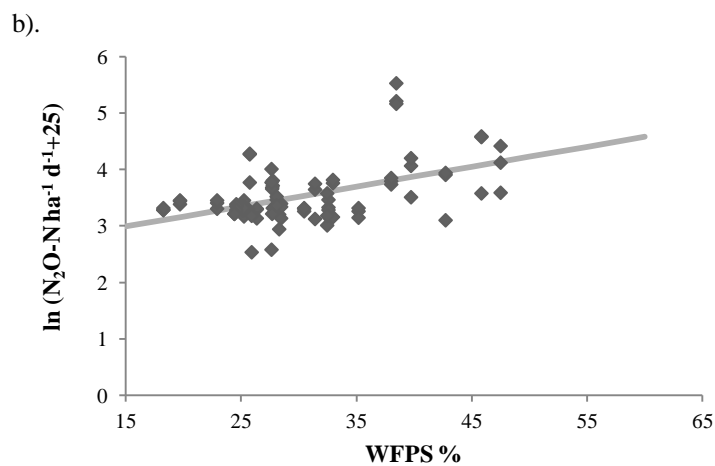
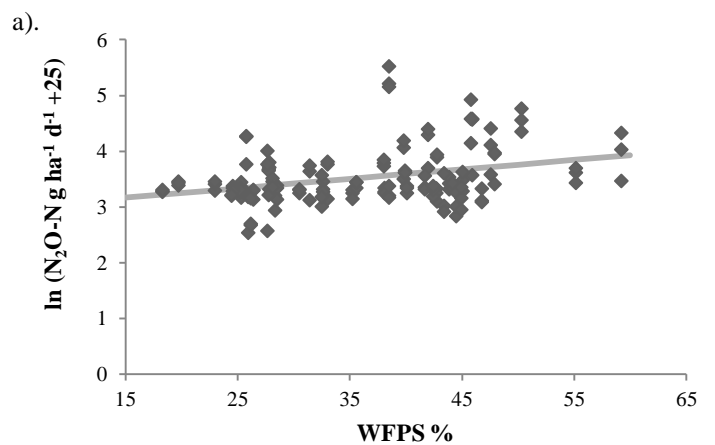
Figure 7. Relationship between average cumulative N_2O flux and average %WFPS (AN 200 kg N ha^{-1}) ($N=3$)

a). Annual relationship (inclusion of all NO_3^- data). $P < 0.001$. $r^2 = 0.18$

$$\ln(N_2O + 25) = 2.907 (\pm 0.1494) + 0.01703 (\pm 0.003998) * wfps$$

b). Seasonal relationship (exclusion of $NO_3^- < 5$ mg/kg). $P < 0.001$ $r^2 = 0.43$

$$\ln(N_2O + 25) = 2.459 (\pm 0.2122) + 0.03538 (\pm 0.006494) * wfps$$



4.3 Emission intensities

Crop yield increased with increasing rates of AN fertiliser application as expected due to the greater availability of NO_3^- and NH_4^+ in the soil for uptake by the growing crop. However, it is important to consider the amount of N_2O produced per unit of yield (yield scaled emissions, or yield intensity). This allows assessment of a greater part of the treatment's "life cycle" than just taking into account N_2O emissions, as ultimately for a fertiliser to be financially viable it must produce sufficient crop yield. The recommended fertiliser application rate of 120 kg N ha^{-1} , which was used in this experiment had yield scaled emissions of $0.39 \text{ kg N}_2\text{O ton}^{-1} \text{ grain}$. The optimum fertiliser application rate would produce a high crop yield but minimal N_2O emissions, and the results of this experiment demonstrate that the optimum fertiliser application would be AN 160 kg N ha^{-1} . This application rate provided a higher crop yield than the 120 kg N ha^{-1} application rate, but lower N_2O emissions, resulting in lower yield scaled emissions of $0.35 \text{ kg N}_2\text{O ton}^{-1} \text{ grain}$. Yield scaled emissions decreased with increasing rates of N fertiliser application at low application rates from $1.15 \text{ kg N}_2\text{O ton}^{-1} \text{ grain}$ for the control treatment to $0.28 \text{ kg N}_2\text{O ton}^{-1} \text{ grain}$ for the AN 80 treatment. Although the yield scaled emissions from the AN 80 treatment are relatively similar to the yield scaled emissions from the optimum AN 160 treatment, it must be considered that crop yields from the AN 160 treatment are 40 % higher, therefore it is advantageous to produce greater crop yields whilst not significantly increasing yield scaled emissions. The yield scaled emission results obtained are in contrast to the results of a meta analysis carried out by Van Groenigen et al. (2010), which reported the lowest emission intensities following N application of $180\text{-}190 \text{ kg N ha}^{-1}$. We found no significant difference in yield scaled emissions from applications of $40\text{-}200 \text{ kg N ha}^{-1}$ despite significantly greater crop yields at N application rates of 160 and 200 kg N ha^{-1} . Our yield scaled emission results indicate that we must avoid under fertilising crops if we are to minimise the risk of enhancing N_2O emissions whilst simultaneously obtaining poor crop yields.

4.4 Mitigation option effects on N₂O emissions and crop yield

The decrease in N₂O emissions through the use of the NI (DCD) is an important finding of this research. The use of DCD has proven effective in reducing N₂O emissions in previous studies conducted on grassland and spring barley sites in New Zealand and the UK (Di and Cameron, 2002, 2003; Di et al., 2007, 2010; McTaggart et al., 1997). However little work has been undertaken to examine the effectiveness of DCD on arable soils in Scotland. A previous field study in the UK investigating the effectiveness of DCD in reducing N₂O emissions from N fertilised arable crops found a 36 % reduction in emissions from spring barley when DCD was used (McTaggart et al., 1997). The successful inhibition of nitrification by DCD in this study is evident due to the significantly increased levels of NH₄⁺-N in the soils from the NI treatments and decreased soil NO₃⁻-N contents, in combination with the decreased N₂O emissions. DCD was more effective in reducing emissions from the AN 120 + NI treatment than from the urea 120 + NI treatment. This is in contrast to previous work which has demonstrated greater decreases in N₂O emissions when DCD was applied to urea fertilised soils in comparison to AN fertilised soils (McTaggart et al., 1997), as would be expected due to the higher quantities of soil NH₄⁺-N found in the urea treatment.

The potential of a 3 split AN fertiliser application and urea application (urea 120) to decrease cumulative N₂O emissions in comparison to the AN 120 treatment was also apparent as emissions were significantly decreased by 11 % and 26 % respectively. The decrease in N₂O emissions associated with the use of a 3 split fertiliser application suggests that the nitrogen use efficiency was increased. However, the mitigation effect was reasonably small and this might be explained by the fertiliser application relatively early in the growing season. The lower N₂O emissions from the urea 120 application in comparison to the AN 120 application is in agreement with the findings of Dobbie and Smith (2003) and Smith et al. (2012). However, the results of this study must be assessed with caution as ammonia (NH₃) emissions were not measured. Smith et al. (2012) reported that 22 % of urea N applied to arable soil is emitted as NH₃, in comparison to <3 % of ammonium nitrate N. The decrease in N₂O emissions associated

with the urea application in this study may therefore be a reflection of greater loss of NH_3 than from the AN treatment resulting in lower soil mineral N concentrations and subsequently decreased potential for N_2O emissions. Evidence for this can be seen in the soil NH_4^+ concentrations where the initially high NH_4^+ concentration in the urea 120 treatment rapidly decreased to lower than the levels seen in the AN 120 treatment, perhaps indicating volatilisation of NH_3 . The decreased N_2O emissions associated with the AN 120 (3 splits) and urea treatments were not associated with increased crop yields as may be expected if greater retention of N within the soil was taking place. Again, this supports the suggestion that considerable quantities of N could have been lost in the form of NH_3 from the urea treatment.

A particularly interesting finding of this research is the significant decrease in crop yield associated with the NI treatments. It was hypothesised that crop yield would be maintained or increased during this experiment due to decreased rates of nitrification and reduced emissions of N_2O and therefore maintenance of higher levels of NH_4^+ in the soil, providing greater N availability for crop growth (Di and Cameron, 2002). However, it has been suggested that plants may preferentially uptake NO_3^- from the soil due to greater ease of transport of NO_3^- through the soil compared with NH_4^+ which is more tightly bound to the soil particles (Hofman and van Cleemput, 2004). If the NI prevented conversion of NH_4^+ to NO_3^- by nitrification, then crop N uptake and growth may suffer. The decrease in crop yield caused by the addition of a NI could have implications for the adoption of NIs as an N_2O mitigation strategy by the farming community, despite the financial benefits for the farmer associated with decreased loss of N through N_2O emissions. The yield results observed in this experiment are in contrast to those demonstrated in previous work in which DCD acted to increase crop or pasture yield (Di and Cameron, 2002; Liu et al., 2013; Pain et al., 1994) or had no effect on crop yield (Weiske et al, 2001). The decrease in N_2O emissions combined with the decrease in crop yield observed from the NI treatments resulted in a large (non significant) reduction in

yield scaled emissions in comparison to the non NI amended treatments by 31 % for the AN 120 + NI treatment and 40 % for the urea 120 + NI treatment.

4.5 Sampling period effects on N₂O emissions and emission factors

This research demonstrated the considerable contribution of background emissions to emissions recorded from applied treatments. Cumulative emissions from the control treatments represent 43 % of annual emissions from the highest N fertiliser treatment and 51 % of emissions from the AN 120 treatment which are within the range of previously reported data. McTaggart et al. (1997) reported background emissions that contributed 75 % of the emissions from spring barley fertilised with 120 kg N ha⁻¹, and Smith et al. (2012) reported 26-67 % contribution of control treatments to emissions from N fertilised treatments. This evidence suggests that background emissions from unfertilised arable crops can be high and represents a considerable proportion of the overall flux from fertilised crops. Smith et al. (2012) suggested that this high background flux from arable sites is due to mineralisation of crop residues which is also likely to have occurred at our experimental site following harvest of the previous oilseed rape crop.

Background emissions could also be considered as those occurring after the return of soil mineral N to background levels, which in this experiment occurred during August 2011. Emissions after this time could reflect crop residue inputs, N deep within the soil profile, remineralised fertiliser N or treatment effects from previous fertiliser events, all of which may confound emissions from the treatments of interest. Our work demonstrated the greatest cumulative monthly emissions in August with mean cumulative N₂O-N emissions of 1.35 kg N₂O-N ha⁻¹. Previous research has often not measured N₂O emissions for an entire year. For example, McTaggart et al. (1997) measured emissions from sowing until early June and although Smith et al. (1998a) measured N₂O emissions for a year from fertilisation, measurements were suspended during a period of low fluxes in the summer and resumed again after autumn cultivation.

If we had not taken measurements during the summer, this period of high emissions would not have been recorded. The large emissions during the summer months are suggested to be due to underlying natural “background” variation in N₂O fluxes over space and time.

Although Bouwman (1996) and the IPCC recommend the use of N₂O emissions data from at least 12 months of measurements in order to calculate EFs to achieve an accurate reflection of management practices, we have calculated EFs over three timescales to analyse the effects of background N₂O emissions on EFs. There were interesting variations between the seasonal and annual EFs with annual EFs (-0.28 – 1.35 %) generally being greater than seasonal EFs (-0.04 – 0.86 %) (Table 2) due to the contribution of emissions over the winter period. Calculating EFs over a longer time period did not always result in a greater EF, for example larger EFs were commonly obtained over the 5 week calculation period in comparison to the seasonal period. This is due to control emissions representing a lower proportion of total emissions immediately following fertiliser application, and the subtraction of these from treatment emissions during the EF calculation thereby causes greater calculated EFs. The question of which EF is more appropriate to use depends on the desired outcome. Our findings indicate that, despite most emissions usually occurring during the 5 week period after fertiliser application, the 5 week EF calculation is inappropriate, when environmental conditions (e.g. rainfall and temperature) after this time period are conducive to N₂O production. This work illustrated that there can be further significant N₂O emissions which should be included in EF calculations to accurately reflect N₂O EFs for arable soils. However, the decision to use a seasonal or annual EF is more complex. If it is desirable to calculate an EF which accurately reflects the effects of specific treatments on N₂O fluxes from arable soils then the results of this work suggest that a seasonal EF should be used in order to remove the effects of background N₂O fluxes which are likely to be unrelated to the applied treatments. Seasonal EFs may therefore provide a more accurate indication of the emissions attributable to fertilisation and specific treatments which makes the use of year long EFs for this purpose questionable. However, this would require removal of a

large part of the data set, which Smith et al. (2012) suggests would usually decrease the magnitude of calculated EFs by 30 % in comparison to those which include a full year's data.

4.6 Comparison to IPCC “default EF” and previously reported values

The mean EFs calculated in this experiment are considerably lower than the IPCC's standard EF1 value of 1.25 % which is currently applied to much of the UK, and also lower than the new EF of 1 %. Mean annual and seasonal EFs were calculated for the purpose of comparison to the IPCC standard value and as such only treatments within the normal range of fertilisation were included (AN 80, AN 120, AN 160, Urea 120). In our study the mean annual EF from these treatments was 0.79 % and the mean seasonal EF was 0.56 %. The EFs of the NI amended treatments were lower than the mean annual EF, due to the decreased N₂O emissions associated with these treatments, however the AN (3 splits) treatment EF was higher than the mean annual EF although lower than the EF of the equivalent AN 120 treatment. The AN 120 treatment is representative of the amount of N fertiliser which would be commercially applied in comparable situations in Scotland. The annual EF for this treatment is 1.35 % which is greater than the IPCC Tier 1 EF of 1.25 % or 1 %. Previous research into EFs from spring barley in Eastern Scotland found EFs of 0.6 - 0.7 % (McTaggart et al., 1997; Smith et al., 1998 a,b), demonstrating a much smaller range of EFs than those found in this experiment. It is suggested that the large range of EFs obtained from this experiment are due to the range of fertiliser application rates, intense sampling frequency and unexpectedly large emissions from the control plots. Also, the unusual weather conditions over the study period which involved large amounts of rainfall over the summer months during which time the treatment effects were no longer occurring, resulted in large emissions which were not associated with individual treatments.

Smith et al. (1998a) compared EFs from Scottish arable and grassland sites to the data plotted by Bouwman (1996) and found that N₂O emissions as a proportion of applied N,

from the Scottish sites, and in particular from the Scottish arable sites, are generally lower than from the rest of the UK. This difference has been suggested to be due to lower temperatures in Scotland resulting in lower N₂O emissions (Smith et al., 1998a). However, if just the EF calculated for the standard fertiliser application rate (AN 120) is considered, then the EF is higher than the IPCC's 1.25 % default EF and the new 1 % EF. Again, this is suggested to be due to the unusual weather conditions experienced during the experimental period. Overall, the range of EFs obtained from this experiment appear to support the movement from the IPCC's 1.25 % EF to the 1 % EF when factors such as the climatic conditions are taken into account. It must also be considered that the experiment was only one year in length, and that to obtain a more accurate view of EFs from these treatments, more experiments of this type would be required in order to take into account variables such as soil and climate.

5. Conclusion

This research demonstrated that area based emissions of N₂O are linearly related to N input, supporting the IPCC's approach to calculating EFs. Soil % WFPS was shown to have a significant effect on the magnitude of N₂O emissions and to have greater control over N₂O production than soil mineral N. For this typical Scottish spring barley crop and soil system receiving mineral fertiliser, the optimum fertiliser application rate is 160 kg N ha⁻¹, as indicated by the calculated N₂O emission intensities of all treatments. Emission intensity results also highlight the need to avoid under-fertilisation of crops if crop yields are to be maintained whilst minimising N₂O emissions. The use of a NI, split fertiliser applications and urea instead of AN, showed the potential to reduce N₂O emissions, however, the amendment of treatments with a NI and 3 split treatment also decreased crop yield, raising questions over their suitability as N₂O mitigation options in arable agriculture and prompting the need for further investigation. The importance of the contribution of background emissions to calculated EFs was demonstrated and the need for year long measurements of N₂O emissions is questioned. Calculated annual EFs were generally lower than the IPCC's default Tier 1 EF of 1.25 % and the new value of 1 %, but largely support movement to, and use of, this new EF value, although further research in other locations is required to assess its suitability for use throughout the UK.

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Chapter 6.

Investigation into the effect of season, form and method of organic fertiliser application on N₂O and NH₃ emissions and emission factors from an arable soil

Investigation into the effect of season, form and method of organic fertiliser application on N₂O and NH₃ emissions and emission factors from an arable soil

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Abstract

Nitrous oxide (N₂O) and ammonia (NH₃) emissions were measured for 18 months from an arable experiment in Eastern Scotland to determine the effects of organic fertiliser application season (autumn vs. spring), form and application method on emissions. Emission factors (EFs) for N₂O and NH₃ were calculated for each treatment and compared to the IPCC's standard N₂O EF of 1.25 % and NH₃ EF of 20 % to assess the appropriateness of using default N₂O and NH₃ EFs regardless of fertiliser type, application season or application method. The treatments tested were farm yard manure (FYM), poultry litter (PL), and layer manure (LM), all of which were surface broadcast. Cattle slurry was applied using a trailing hose application (STH) or surface broadcast (SSB). Application rates varied between 50-244 kg N ha⁻¹ and plots were sown with winter wheat. Treatments were applied in October 2012 and April 2013, to test the effect of application season on N₂O and NH₃ emissions. Emissions of N₂O were measured using the static closed chamber technique and NH₃ emissions were measured using wind tunnels. Crop yield was recorded at harvest to allow calculation of N₂O and NH₃ emission intensities. Cumulative N₂O emissions as a % of N applied from the autumn applications were greater than those from the spring with maximum cumulative autumn emissions of 4.07 % from the STH and maximum cumulative spring emissions as a % of N applied of 0.69 % from the PL. Differences in N₂O emissions between treatments

were more evident from the autumn treatments. Ammonia emissions were generally greater from spring applications in comparison to autumn with maximum cumulative spring NH_3 emissions as a % of N applied of 19.18 % from the SSB. There was no effect of fertiliser application method on N_2O and NH_3 emissions, or crop yield and yield scaled emissions. The lowest yield scaled emissions from the autumn application were 0.61 and 1.60 kg $\text{N}_2\text{O-N} + \text{NH}_3\text{-N ton}^{-1}$ grain from the FYM and PL treatments respectively, and 0.37, 2.09 and 2.82 kg $\text{N}_2\text{O-N} + \text{NH}_3\text{-N ton}^{-1}$ grain from the CON, STH and SSB treatments respectively from the spring application. N_2O EFs ranged between -1.10 % from the spring SSB to 2.78 % from the autumn STH. The NH_3 EFs ranged between 0.39 % from the autumn FYM to 19.18 % from the spring SSB. The results of this experiment demonstrate the considerable effect of choice of organic fertiliser and application season on N_2O and NH_3 emissions and the need for EFs to take these into account.

6.1 Introduction

Organic materials such as manure and slurry are commonly used as fertilisers in arable agriculture due to their ability to provide large quantities of nitrogen (N) required for crop growth. The application of these products to land also offers benefits in the form of reduced use of inorganic fertilisers and improved soil quality through the addition of organic matter to the soil (Defra, 2010). However, considerable amounts of fertiliser N will never be utilised by the crop as a result of mineralisation, immobilisation, nitrification and denitrification transformations in the soil and subsequent emission of nitrous oxide (N_2O) and dinitrogen (N_2) gases. Organic fertiliser applied N is also lost through ammonia (NH_3) volatilisation and leaching of the nutrients nitrate (NO_3^-) and ammonium (NH_4^+) into groundwater and as runoff into waterways (Rodhe et al., 2006). N_2O is a powerful greenhouse gas (GHG) with a global warming potential 298 times greater than that of CO_2 and also depletes the stratospheric ozone layer (Stocker et al., 2013). At the global scale 65 % of anthropogenic N_2O emissions originate from soil (Reay et al., 2012). Volatilised NH_3 is deposited and NO_3^- is transported into aquatic or terrestrial environments resulting in indirect N_2O loss and environmental impacts such as eutrophication and soil acidification. It has been estimated that 92 % of the UK's anthropogenic NH_3 emissions and 73 % of the UK's anthropogenic N_2O emissions are from land management sources (Dore et al., 2008; Skiba et al., 2012).

The potential for emission of N_2O and NH_3 after application of organic fertilisers to agricultural soils is dependent on a combination of contributory factors including fertiliser properties and environmental conditions. High temperatures, high windspeed and low rainfall immediately following fertiliser application are all conditions which promote large emissions of NH_3 (Meisinger and Jokela, 2000). The N content of organic fertilisers, and the proportion of N in the form of readily available N (ammonium-N or uric-N) or organic N varies in relation to the type of organic fertiliser (Defra, 2010; Shepherd and Newell-Price, 2013). Large quantities of readily available N (35-70 % of

total N) are typically found in slurries and poultry manures in comparison to the relatively small quantity of readily available N (10-25 % of total N) found in farmyard manure (FYM) (Defra, 2010). The quantity of readily available N in organic fertilisers affects the potential for loss of N from the soil system through NH_3 volatilization, N_2O emissions, or leaching of NO_3^- , with greater probability of N loss from fertilisers containing large amounts of readily available N (Defra, 2010). The dry matter or moisture content of the organic fertiliser may affect the potential for emissions of N_2O from the soil as increased soil moisture can result in enhanced production of N_2O with the greatest N_2O emissions occurring between 50-70 % WFPS (Flechar et al., 2007). Slurry can have a moisture content of >90 %, which increases the risk of high N_2O emissions after application (Jorgensen et al., 1998). The moisture content of organic fertilisers also affects the rate at which NH_3 emissions occur. Slurries with a high moisture content generally have high emissions of NH_3 in the 12 hours following application, which then rapidly decline. Poultry litter which has a lower moisture content than slurry has a lower initial loss of NH_3 following application but emissions occur over a longer timescale (Jones et al., 2007; Meisinger and Jokela, 2000). The C/N ratio of organic fertilisers may also affect the loss of N from the soil system. Akiyama et al. (2004) suggested that the higher C/N ratios of organic fertilisers in comparison to chemical fertilisers provided optimum conditions for denitrification to occur following application as the source of C increased microbial activity thereby creating anaerobic conditions. This allowed denitrification to occur at lower % WFPS than for chemical fertilisers, thus enhancing the risk of N_2O production (Akiyama et al., 2004).

The timing of organic fertiliser application can also be critical if significant losses of N from the soil system are to be avoided. Ammonia volatilization from soils to which organic fertiliser containing large quantities of readily available N has been applied is generally increased when application occurs in warm conditions, and to dry soils (Defra, 2010). Conversely, loss of N via NO_3^- leaching and N_2O emission is higher when organic fertiliser is applied in wet conditions as leaching of NO_3^- and production of N_2O

via denitrification will occur before the crop is able to utilise the available N (Defra 2010; Shepherd and Newell Price, 2013). In order to reduce losses of N it is generally recommended that organic fertilisers should be applied when weather conditions are drier and cooler or in periods when crops are actively growing and removing N from the soil (Defra, 2010; Granli and Bockman, 1994; Meisinger and Jokela, 2000). The application of organic fertilisers during the autumn and winter periods in many areas of the UK is restricted by Nitrate Vulnerable Zone (NVZ) regulations which aim to decrease nitrate pollution of aquatic environments from agricultural sources but will also assist in decreasing N₂O emissions (The Scottish Government, 2014). Diurnal trends in NH₃ emissions are also evident, with greater losses during the day time than at night, promoting evening applications as a potential mitigation option (Meisinger and Jokela, 2000). To minimise the effects of timing of application on losses of N from the system, it is suggested that the chosen application timing should try to provide a balance between the need to apply fertiliser during the period of maximum crop N requirement but also the need to reduce seasonal climate effects on emissions (Meisinger and Jokela, 2000). Reducing losses of N from the soil is beneficial for crop growth as more N is available for use by the growing crop (Defra, 2010; Rodhe et al., 2006).

The method of organic fertiliser application is also crucial when considering N loss and subsequent environmental impacts. Placement of the organic fertiliser lower down the soil profile has generally been found to reduce NH₃ emissions in comparison to surface applications (Rodhe et al., 2006; Wulf et al., 2001). Wulf et al. (2001) compared NH₃ emissions from a range of slurry application techniques to arable soil and found that injecting slurry reduced NH₃ emissions by around two thirds in comparison to trailing hose application, which was also less effective at reducing NH₃ emissions than incorporation of slurry following trailing hose application. Different types of surface application also affect the magnitude of NH₃ emissions. Misselbrook et al. (2002) compared NH₃ emissions from application of slurry to arable land by surface broadcast and bandspread application and found a 27 % reduction in emissions from the

bandsread technique, with the majority of the difference occurring due to a reduction in maximum emissions in the first few hours following application. Despite the benefits associated with reduced NH_3 emissions due to placement of the slurry within the soil profile, various studies have reported significantly increased N_2O emissions following injection of slurry in comparison to surface application due to increases in soil moisture and denitrification rates (Chadwick et al., 2011; Perala et al., 2006; Wulf et al., 2001).

The amount of N_2O or NH_3 emitted from N fertilised soils can be expressed in terms of an emission factor (EF). This defines the quantity of N_2O or NH_3 emitted as a proportion of the total N applied (after background emissions have been subtracted). The UK currently uses the IPCC's Tier 1 methodology for calculating EFs and this states that N_2O emissions from soils receiving organic amendments are equal to 1.25 % of the fertiliser N applied (IPCC, 1996), and that NH_3 emissions from soils receiving organic amendments are equal to 20 % of the total N applied (IPCC, 2006). The N_2O EF has been revised to give an EF of 1 % of fertiliser N applied (IPCC, 2006), and the UK will begin to use this EF in 2015. These EFs are used to estimate N_2O and NH_3 emissions from locations throughout the UK to enable compilation of agricultural N_2O and NH_3 emissions inventories. The EF calculations do not take into account locally variable factors such as soil type or climate, or variations in the form of fertiliser used, or the season or method of application, all of which can influence the magnitude of N_2O and NH_3 emissions. Research into the effects of these variables on the production of N_2O and NH_3 is necessary if the accuracy of N_2O and NH_3 emissions reporting is to be improved.

Due to the variety of conditions which affect N loss from soils amended with organic fertiliser, it is imperative that organic fertiliser is carefully managed through all stages from production to application, if significant environmental pollution is to be avoided. It is thus vital to understand how manipulation of the form, timing and application method

of organic fertiliser applications may reduce potential environmental impacts. The results of this research which forms part of a nationwide project, will contribute to reducing uncertainty in the UK's agricultural GHG inventory, and will enhance the sustainability and GHG mitigation potential of farming systems (GHG, 2013).

This research aims to:

- i) Compare emissions of N_2O and NH_3 from the application of organic fertilisers including cattle slurry, farmyard manure, poultry litter and layer manure.
- ii) Investigate the effect of fertiliser application season on N_2O and NH_3 emissions by comparing emissions from spring and autumn fertiliser applications.
- iii) Investigate the effect of the method of fertiliser application on N_2O and NH_3 emissions by comparing surface broadcast and trailing hose applications.
- iv) Determine any effects of the timing, form and method of fertiliser application on crop yield and N uptake.
- v) Assess the effect of the timing, form and method of fertiliser application on calculated N_2O and NH_3 EFs.

6.2 Materials and methods

6.2.1 Site description and experimental design

An 18 month field trial was established at an arable farm in East-central Scotland in autumn 2012 on a sandy loam soil with a pH of 6 and organic matter content of 6 %. Prior to this experiment, the field had been sown with a spring barley crop for the previous four years. The site was at 190 m a.s.l and had a 40 year (1955-1995) mean annual precipitation of 849 mm and mean daily temperatures in July and January of 13.3 and 3.8°C, respectively. The site is <1 km outside the Nitrate Vulnerable Zone (NVZ) regulation area. The experiment took place within a single field, however, two blocks of experimental plots were established, located within a few metres of each other on flat ground of the same soil type. One of these blocks was designated the “autumn fertiliser application block” and contained all of the autumn applied treatments, and the other block was the “spring fertiliser application block” and contained all of the spring applied treatments. Due to field operations e.g. drilling, spraying and harvesting, it would have been impossible to establish the autumn and spring treatments within the same block. Each block had a randomized design including a control, with treatments replicated three times on plots (12 m x 6 m). Measurements from the autumn applied treatments were taken from the “autumn fertiliser application block” and were compared to other autumn applied treatments within the same block, the same was done for spring treatments in the “spring fertiliser application block”. Both areas were sown with winter wheat (v. Grafton), a typical crop for the area, on 25th October 2012 at a seed rate of 400 m⁻². Organic fertiliser treatments comprising farmyard manure (FYM), poultry litter, layer manure, and cattle slurry were applied, all of which are livestock wastes commonly applied to Scottish farmland. The target application rate for available-N in all treatments was 180 kg N ha⁻¹, although actual rates were variable (Table 1), due to varying N contents and application practicalities. All treatments were applied using methods common in this locality. Appropriate quantities of fertilisers were obtained to permit over winter storage of the fertiliser remaining after the autumn applications, prior to their application the following spring. Details of treatments can be found in Table 1.

Throughout the experiment, pesticides and herbicides were applied following the farmer's recommendations, to meet crop growth requirements.

Table 1. Organic fertiliser application rates and properties at time of application and application timings

Treatments	Total N applied (kg N ha ⁻¹)	Readily available N applied (kg N ha ⁻¹)	Dry matter %	pH	Total N (mg kg ⁻¹)	NH ₄ ⁺ -N (mg kg ⁻¹)	NO ₃ ⁻ -N (mg kg ⁻¹)	Uric acid N (mg kg ⁻¹)	Total C (mg kg ⁻¹)	C/N ratio
Control (CON)	0									
Farmyard manure (FYM)	A : 175 S : Not applied	A : 5 S : *	A : 18.4 S : *	A : 8.35 S : *	A : 5900 S : *	A : 180 S : *	A : 110 S : *	A : * S : *	A : 367000 S : *	A : 6.22 S : *
Poultry litter (PL)	A : 141 (i). S : 121	A : 12 S : 24	A : 41.6 S : 26.6	A : 8.29 S : 8.85	A : 24800 S : 15000	A : 2130 S : 2800	A : <100 S : <100	A : * S : 230	A : 364000 S : 340000	A : 14.67 S : 22.67
Layer manure (LM)	A : 244 (i). S : 228	A : 121 S : 91	A : 21.8 S : 21.8	A : 7.99 S : 8.60	A : 16700 S : 13900	A : 8250 S : 5570	A : <100 S : <100	A : * S : 370	A : 315000 S : 311000	A : 18.86 S : 22.37
Cattle slurry (broadcast) (SSB)	A : 63 (i). S : 50	A : 30 S : 20	A : 2.3 S : 1.6	A : 6.84 S : 6.89	A : 1500 S : 1100	A : 730 S : 530	A : <100 S : <100	A : * S : *	A : 349000 S : 5264	A : 232.67 C : 4.79
Cattle slurry (trailing hose) (STH)	A : 63 (i). S : 50	A : 30 S : 20	A : 2.3 S : 1.6	A : 6.84 S : 6.89	A : 1500 S : 1100	A : 730 S : 530	A : <100 S : <100	A : * S : *	A : 349000 S : 5264	A : 232.67 C : 4.79

A= Autumn Application

S= Spring application

(i)= treatment incorporated after 24 hours

*=data unavailable

6.2.2 Measurements and analysis

Fifteen measurements (five measurements in each of the three replicate plots) of N₂O were taken from each treatment on each sampling occasion using the static closed chamber technique (Clayton et al., 1994) and methods used were consistent with the Global Research Alliance guidelines (de Kleine and Harvey, 2012). Five opaque plastic chambers each covering a soil area of approximately 0.16 m² were inserted to a soil depth of 5 cm on each plot, resulting in the use of 15 chambers per treatment. The chambers remained in situ for the entire experiment with the exception of removal when agricultural operations were taking place. An intensive sampling strategy was adopted immediately after fertiliser application to capture N₂O fluxes from the period of high emissions, with the frequency of sampling decreasing with time. In total, N₂O fluxes were measured on 64 occasions during the 18 month experimental period. On each sampling occasion the chambers were closed for 40 minutes and gas samples were taken using a syringe through a sampling port in the chamber lids. Sampling was conducted between 10:00 and 12:00h to ensure consistency and minimise the effects of diurnal fluctuation. Ambient gas samples were collected on every gas sampling occasion and the linearity of gas accumulation within the chambers was also checked, following the method described by Chadwick et al. (2014). N₂O concentrations of gas samples collected in pre-evacuated glass vials were determined using gas chromatography (Agilent 7890A Gas Chromatograph) (GC) fitted with an electron capture detector (Agilent Technologies, Berkshire, UK) and a CTC Analytics COMBI PAL autosampler (CTC Analytics, Hampshire, UK). Daily N₂O fluxes were calculated using linear regression and cumulative N₂O fluxes were calculated using the trapezoidal rule. The use of a large number of chambers per treatment, combined with the intensive N₂O sampling strategy was designed to take into account the high spatial and temporal variability of N₂O emissions from soils, allowing more reliable estimates of N₂O fluxes from each treatment than has been obtained previously in similar experiments [e.g. Smith et al., 2012 ; Dobbie and Smith, 2003].

Ammonia emissions from organic fertiliser treatment plots were measured using small scale wind tunnels and absorption of NH_3 in orthophosphoric acid (Misselbrook et al., 2005). The wind tunnels consisted of a transparent polycarbonate canopy (2 m x 0.5 m) which was placed over part of the plot area, with air drawn through the canopy at 1 ms^{-1} by a fan in a stainless steel duct. The plots were orientated at 20 degrees to the vertical, and at 90 degrees to the prevailing wind. The wind tunnels were positioned on the plots, in the direction of the prevailing wind and in a suitable position so as to avoid air entering the wind tunnel from adjacent plots. Subsamples of the air from the canopy inlet and outlet were passed through absorption flasks containing 80 ml of 0.02 M orthophosphoric acid. On each sampling occasion the flasks of orthophosphoric acid were changed and concentrations of NH_3 in inlet and outlet orthophosphoric acid samples were determined using colorimetric analysis (Misselbrook et al., 2005). One wind tunnel was placed on each plot and NH_3 emissions were measured daily for 7 days from the slurry and FYM treatments, and for 14 days from the poultry treatments, accounting for expected differences in the timescales of NH_3 emissions from these treatments (Meisinger and Jokela, 2000).

On each N_2O sampling occasion, 5 soil samples (0-10 cm depth) were collected from each block and combined for soil gravimetric water content (GWC) determination. Each month, 5 soil samples were also collected from each plot and combined, before being sieved (<4 mm) and extracted using 2 M KCl to determine plot average soil ammonium ($\text{NH}_4^+\text{-N}$) and nitrate ($\text{NO}_3^-\text{-N}$) contents using a Skalar San⁺⁺ continuous flow autoanalyser (Skalar, York, UK). Metal rings were used to collect intact soil samples for soil bulk density measurement at regular intervals throughout the experiment. The soil bulk density measurements and GWC were then used to calculate soil water filled pore space (WFPS).

A weather station was used to record daily climatic conditions, and soil and air temperatures were measured on each N₂O sampling occasion (RS Components, Northamptonshire, UK). Winter wheat was harvested on 5th September 2013 using a small plot harvester, with the yield from a 15 m² area recorded for each plot. Additional samples of 100 tillers from each plot were collected manually to determine the ratio of grain to straw and chaff. The crop yield and the N content and % dry matter of the grain, straw and chaff was recorded. Crop N analysis was carried out using a Carlo Erba NA 2500 Elemental Analyser.

Losses of N via nitrate leaching from the autumn applied treatments were measured from each plot, using 5 replicate porous ceramic pots. However, due to delays in installing the porous pots, the nitrate leaching data is not included in this manuscript.

6.2.3 Emission factor calculations

Annual N₂O and NH₃ EFs were calculated (subtracting control values from each of the 3 blocks from corresponding block treatment values, before calculating mean treatment EFs) using the following equation:

N_x EF:

$$\text{Cumulative N}_x \text{ flux from N applied (kg N}_x\text{-N)} - \text{Cumulative N}_x \text{ flux from control (kg N}_x\text{-N)} * 100 / \text{N applied (kg N)}$$

Where x is N₂O or NH₃.

NH₃ emissions were not measured from the control plots and for the purposes of calculating EFs were assumed to be zero. This is a common approach in the literature and has been used in many studies including Misselbrook et al. (2002), Wolf et al. (2014) and Wulf et al. (2001). This is due to low background atmospheric concentrations of NH₃, with reported mean annual background values of < 1 µg m⁻³ (Vogt et al. 2013).

6.2.4 Calculation of indirect N₂O emissions

Indirect N₂O emissions from NH₃ volatilisation and nitrate leaching were estimated. Indirect N₂O emissions may occur following the volatilization of NH₃, after which deposition of NO₃⁻ or NH₄⁺ into terrestrial or aquatic ecosystems may occur, resulting in potential transformation into N₂O. Nitrous oxide emissions from this source are estimated to be 1 % of the volatilized NH₃-N (IPCC, 2006). Indirect N₂O emissions associated with leaching losses of N were also calculated. 30 % of applied N is estimated to be lost via leaching, and 0.75 % of the leached N is estimated to be re-emitted as N₂O (IPCC, 2006).

6.2.5 Statistical analysis

Statistical analysis of the data was carried out using Minitab (16th edition). Analysis of variance (ANOVA) and Tukey's multiple comparison test were used to test for significant differences between treatments. Regression analysis was used to test for a relationship between cumulative N₂O emissions and the readily available N content of applied fertilisers. Significance was assumed if $p \leq 0.05$.

6.3 Results

6.3.1 Nitrous oxide fluxes and emission factors

Temporal variation in N₂O fluxes showed different trends following the autumn application and the spring application. There was a large peak in N₂O emissions from all autumn applications 9 days after fertiliser application in October 2012, with the greatest peak in emissions of 148 g N₂O-N ha⁻¹ d⁻¹ from the SSB treatment. N₂O emissions then declined rapidly and remained <50 g N₂O-N ha⁻¹ d⁻¹ for the remainder of the experiment (Figure 1a). N₂O emissions following the spring application did not demonstrate a single large peak in emissions but were characterised by small emissions which continuously fluctuated throughout the measurement period. The maximum daily peak in emissions of 20 g N₂O-N ha⁻¹ d⁻¹ was observed from the LM treatment in August 2013, after which all N₂O emissions remained <5 g N₂O-N ha⁻¹ d⁻¹ (Figure 1b).

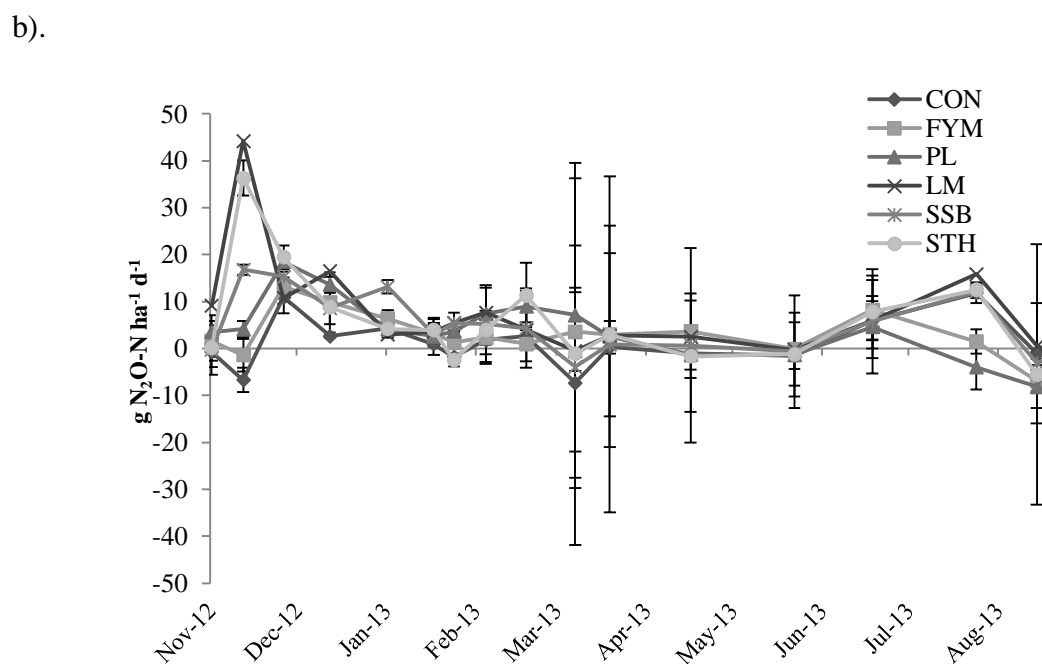
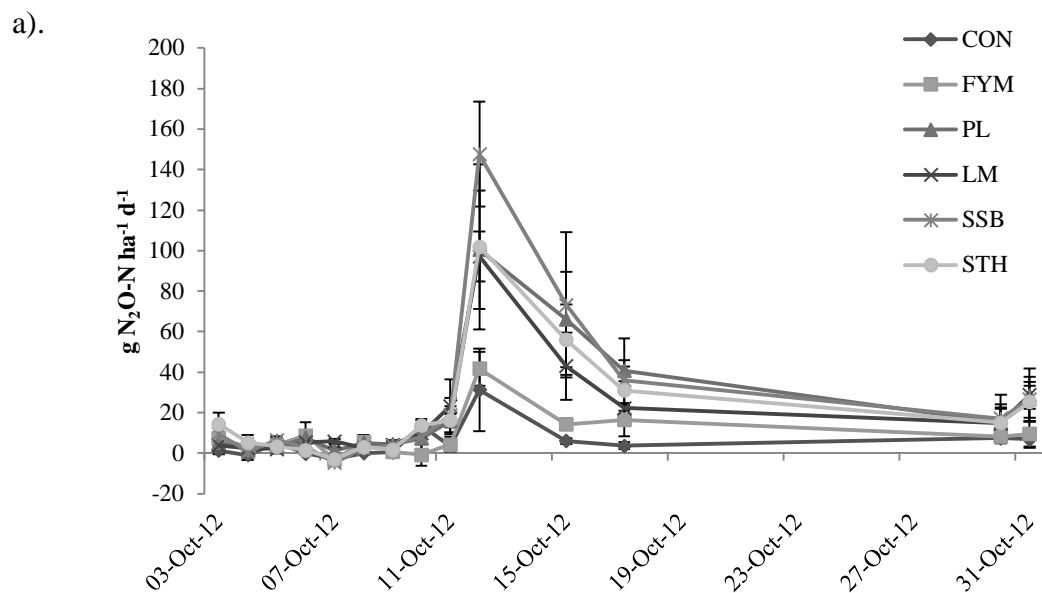
Cumulative N₂O emissions from the autumn applications ranged from a minimum of 0.81 kg N₂O-N ha⁻¹ from the CON treatment to 2.91 kg N₂O-N ha⁻¹ from the LM treatment (Table 2). There were no significant differences in cumulative N₂O emissions between any treatments in the autumn application experiment. The STH treatment demonstrated the greatest cumulative N₂O emissions as a % of N applied with a value of 4.07 % which was significantly greater than the 0.77 % obtained from the FYM treatment. There were no other significant differences between treatments. The spring applications showed a range in cumulative N₂O emissions from -0.12 kg N₂O-N ha⁻¹ from the SSB treatments to 0.85 kg N₂O-N ha⁻¹ from the LM treatment (Table 2). Maximum N₂O emissions as a % of N applied were recorded from the PL treatment with a value of 0.69 %. There were no significant differences in cumulative N₂O emissions or N₂O emissions as a % of N applied between any treatments. There was no significant relationship ($p>0.05$) between the readily available N content of the applied fertilisers and cumulative N₂O emissions after the first month, or full year, of measurements.

Cumulative N₂O emissions and N₂O losses as a % of N applied were greater from the autumn treatments than the spring treatments, with significantly greater autumn cumulative N₂O emissions from all treatments except the control ($p < 0.05$) and significantly greater autumn N₂O losses as a % of N applied from all treatments except the control and LM ($p < 0.05$). The greatest difference between autumn and spring cumulative N₂O emissions was 2.63 kg N₂O-N ha⁻¹ from the SSB treatments (Figure 2). The SSB treatment also demonstrated the greatest difference in N₂O loss as a % of N applied between the autumn and spring treatments, with a difference of 4.22 % (Figure 2).

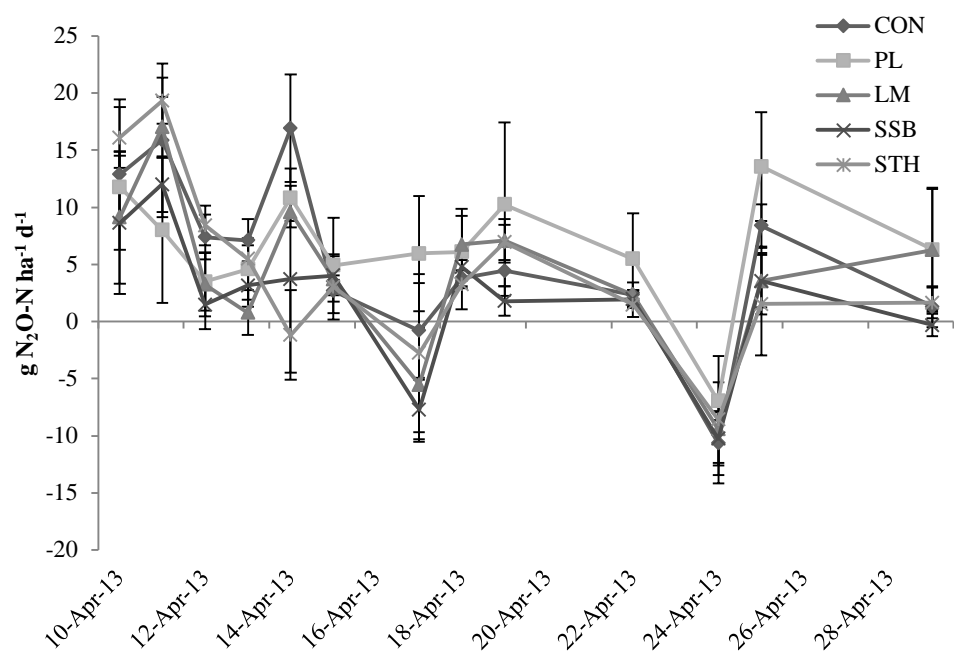
Annual N₂O EFs for the autumn applications ranged from 0.31 for the FYM treatment to 2.78 from the STH treatment. Smaller EFs were obtained from all spring applications with a maximum EF of 0.34 from the PL treatment and a minimum EF of -1.10 from the SSB (Table 2). The mean N₂O EF for autumn and spring treatments combined was 0.65, the mean N₂O EF for the autumn treatments was 1.49 and for the spring treatments was -0.39.

Figure 1. (a) Daily N_2O emissions from autumn treatments during October 2012 (b) Daily N_2O emissions from autumn treatments between November 2012 to August 2013 (c) Daily N_2O emissions from spring treatments during April 2013 (d) Daily N_2O emissions from spring treatments between May 2013 to December 2013.

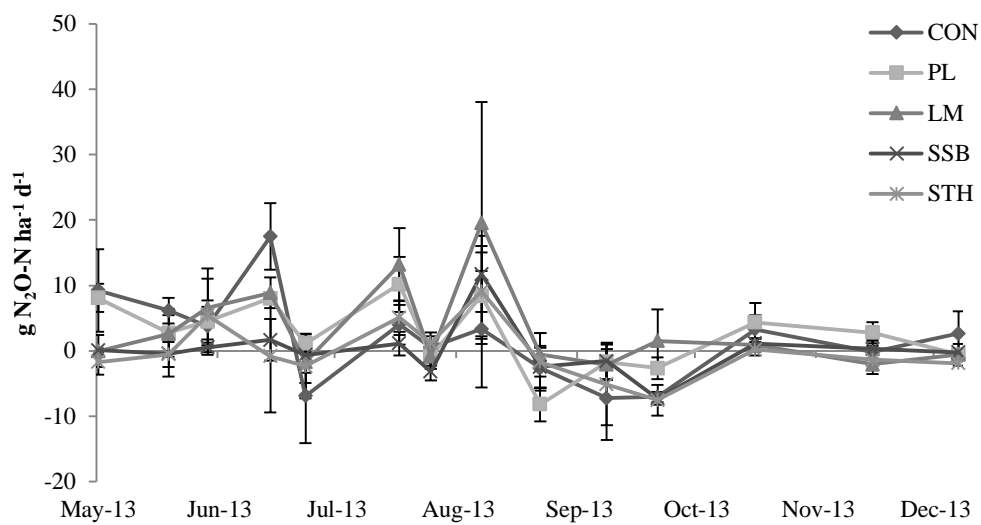
Hourly NH_3 emissions from autumn treatments (c) and spring treatments (d) covering measurement periods of 336 hours (14 days).



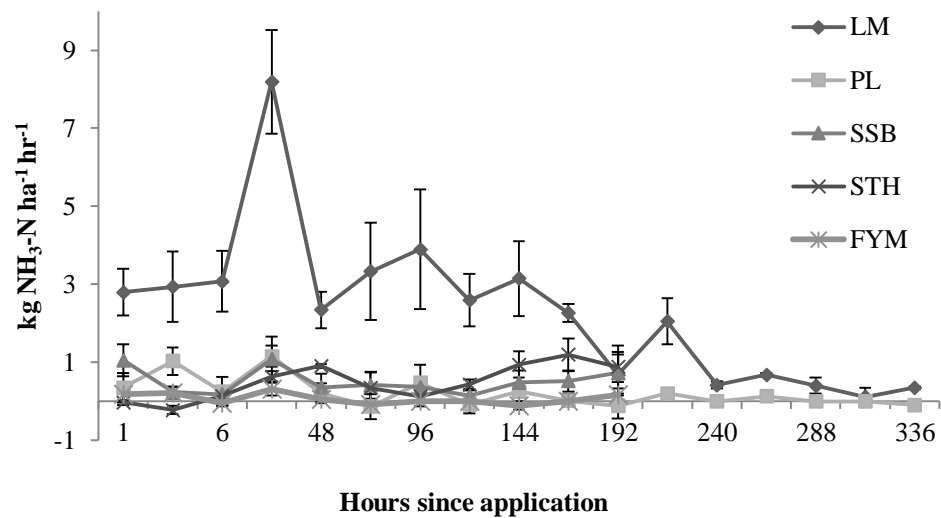
c).



d).



e).



f).

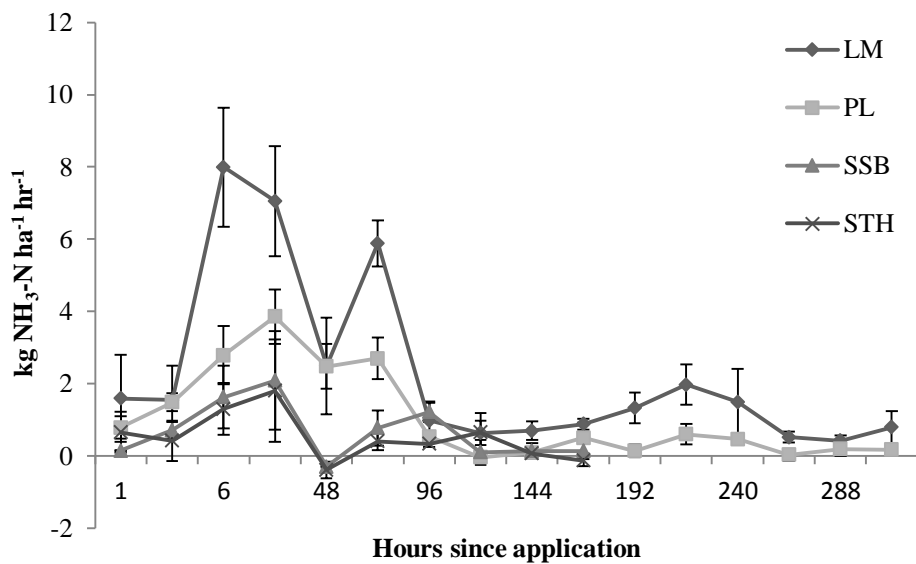


Table 2. Cumulative direct N₂O and NH₃ emissions, indirect N₂O emissions, % N applied and EFs for each treatment

Treatment	Cumulative N ₂ O emissions (kg N ₂ O-N ha ⁻¹)	N ₂ O emissions as % N applied	N ₂ O EF %	Cumulative NH ₃ emissions (kg NH ₃ -N ha ⁻¹)	NH ₃ emissions as % N applied	NH ₃ EF %	Total N loss as % N applied	Indirect N ₂ O emissions (kg N ₂ O-N)	Total direct and indirect N ₂ O emissions (kg N ₂ O-N)
CON	A: 0.81 ^b S: 0.40 ^b	A: * S: *	A: * S: *	A: * S: *	A: * S: *	A: * S: *	A: * S: *	A: * S: *	A: * S: *
PL	A: 1.95 ^b S: 0.84 ^c	A: 1.38 ^b S: 0.69 ^c	A: 0.81 S: 0.34	A: 3.60 ^b S: 17.85 ^c	A: 2.56 ^b S: 14.75 ^c	A: 2.56 S: 14.75	A: 3.93 ^b S: 15.45 ^c	A: 0.35 S: 0.45	A: 2.30 S: 1.29
LM	A: 2.91 ^b S: 0.85 ^c	A: 1.19 ^b S: 0.37 ^b	A: 0.86 S: 0.18	A: 39.23 ^b S: 36.86 ^b	A: 16.03 ^b S: 16.17 ^b	A: 16.03 S: 16.17	A: 17.22 ^b S: 16.54 ^b	A: 0.94 S: 0.88	A: 3.85 S: 1.73
SSB	A: 2.51 ^b S: -0.12 ^c	A: 3.98 ^b S: -0.24 ^c	A: 2.69 S: -1.10	A: 5.54 ^b S: 9.59 ^b	A: 8.86 ^b S: 19.18 ^b	A: 8.86 S: 19.18	A: 12.84 ^b S: 18.94 ^b	A: 0.20 S: 0.21	A: 2.71 S: 0.09
STH	A: 2.56 ^b S: -0.06 ^c	A: 4.07 ^b S: -0.13 ^c	A: 2.78 S: -0.99	A: 5.33 ^b S: 6.01 ^b	A: 8.53 ^b S: 12.03 ^b	A: 8.53 S: 12.03	A: 12.60 ^b S: 11.90 ^b	A: 0.20 S: 0.17	A: 2.76 S: 0.11
FYM	A: 1.35 S: *	A: 0.77 S: *	A: 0.31 S: *	A: 0.69 S: *	A: 0.39 S: *	A: 0.39 S: *	A: 1.16 S: *	A: 0.40 S: *	A: 1.75 S: *

A= autumn application

S= spring application

Different letters (b,c) after the value represents significant difference in emissions from the same treatment applied at different times (p<0.05)

*= no data available

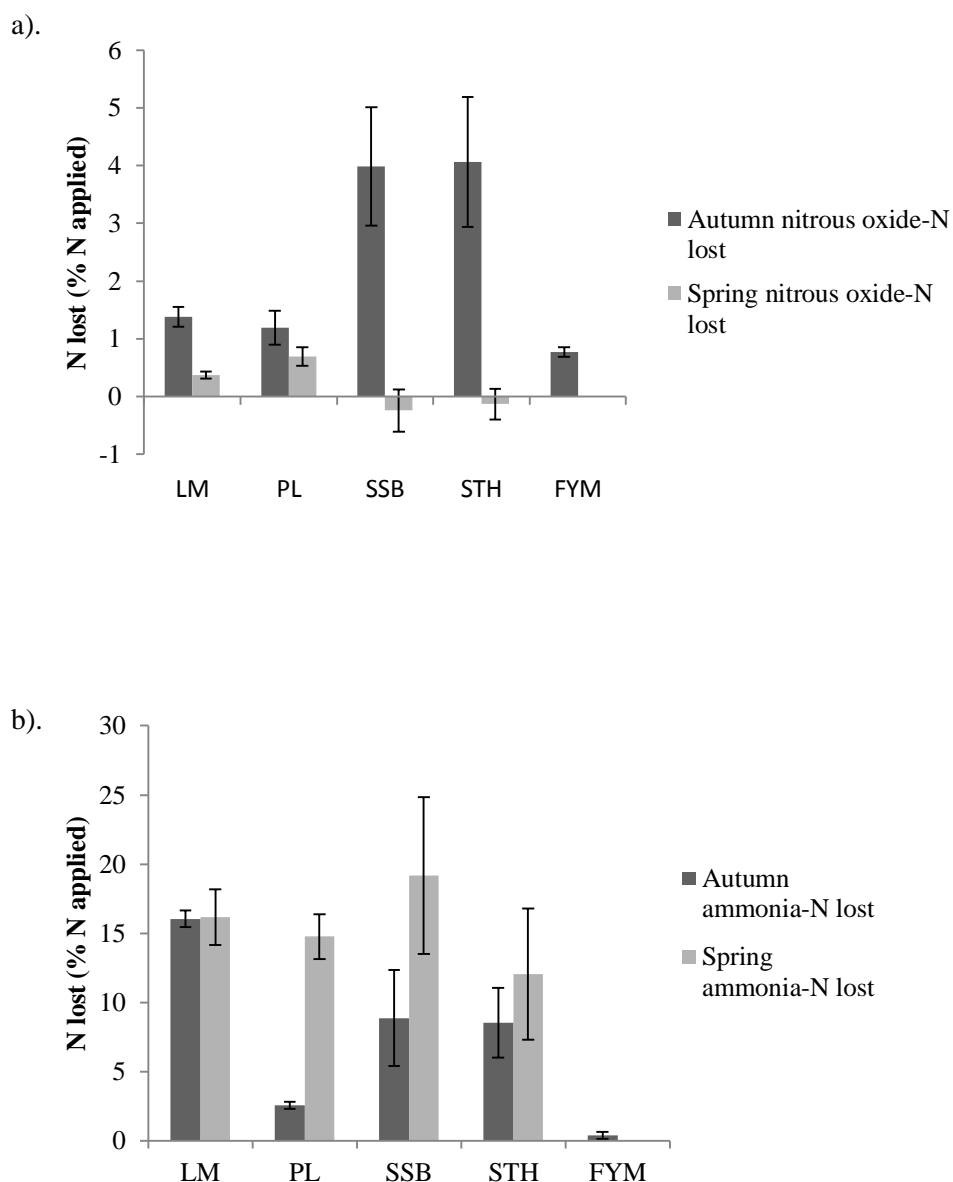
6.3.2 Ammonia fluxes and emission factors

Emissions of NH_3 from the autumn fertiliser applications were consistently $< 2 \text{ kg NH}_3\text{-N ha}^{-1} \text{ hr}^{-1}$ throughout the measurement period from all treatments except the LM. There was a large peak in NH_3 emissions of $8 \text{ kg NH}_3\text{-N ha}^{-1} \text{ hr}^{-1}$ from the LM treatment 24 hours after fertiliser application (Figure 1). Emissions from the LM treatment then gradually declined to $<4 \text{ kg NH}_3\text{-N ha}^{-1} \text{ hr}^{-1}$ for the remainder of the measurement period. NH_3 emissions from the spring applications showed more fluctuation than the autumn emissions. Emissions from all treatments increased following fertiliser application with the maximum peak in emissions of $8 \text{ kg NH}_3\text{-N ha}^{-1} \text{ hr}^{-1}$ from the LM treatment occurring 6 hours after application and maximum peaks from all other treatments occurring 24 hours after application, with maximum emissions of $4 \text{ kg NH}_3\text{-N ha}^{-1} \text{ hr}^{-1}$ from the PL treatment (Figure 1). NH_3 emissions from all treatments then declined, and remained $<2 \text{ kg NH}_3\text{-N ha}^{-1} \text{ hr}^{-1}$, except for a small peak in emissions 72 hours after fertiliser application.

Cumulative NH_3 emissions from the autumn applications ranged from $0.69 \text{ kg NH}_3\text{-N ha}^{-1}$ for the FYM treatment to $39 \text{ kg NH}_3\text{-N ha}^{-1}$ from the LM (Table 2). Cumulative $\text{NH}_3\text{-N}$ emissions from the LM were significantly greater than from all other treatments ($p<0.01$). The LM treatment also showed the largest NH_3 emissions as a % of N applied with a maximum value of 16 % which was significantly higher ($p<0.05$) than the values of 2.56 % and 0.39 % obtained from the PL and FYM treatments, respectively (Figure 2). Cumulative NH_3 emissions from the spring treatment ranged from $6 \text{ kg NH}_3\text{-N ha}^{-1}$ from the STH treatment to $37 \text{ kg NH}_3\text{-N ha}^{-1}$ from the LM treatment, with significantly greater emissions from the LM treatment than from all other treatments ($p<0.01$) (Table 2). Maximum NH_3 emissions as a % of N applied were obtained from the SSB treatment with a value of 19 % (Figure 2). There were no significant differences in NH_3 emissions as a % of N applied between any of the spring treatments. There were significantly greater cumulative NH_3 emissions and NH_3 emissions as a % of N applied from the spring PL treatment in comparison to the autumn PL treatment (Table 2).

Autumn NH_3 EFs were smaller than spring NH_3 EFs with autumn NH_3 EFs ranging from 0.39 from the FYM to 16.03 from the LM, and spring NH_3 EFs ranging from 12.03 for the STH to 19.18 for the SSB (Table 2). The mean autumn NH_3 EF was 7.3 and the mean spring NH_3 EF was 15.5. The mean overall NH_3 EF for autumn and spring treatments combined was 10.9.

Figure 2. NH_3 and N_2O emissions from each treatment as % N applied **a).** N_2O -N lost as % N applied from autumn and spring applications **b).** NH_3 -N lost as % N applied from autumn and spring applications.



6.3.3 Total N loss as % N applied

Total N loss as a % of N applied (combined total $\text{NH}_3\text{-N}$ and $\text{N}_2\text{O-N}$ loss as a % of N applied) from the autumn treatments ranged from a minimum of 1 % from the FYM to 17 % from the LM (Table 2). There were significantly ($p<0.01$) greater amounts of total N loss as a % of N applied from the autumn LM, SSB and STH treatments in comparison to the autumn PL and FYM treatments. There was no significant difference between the autumn SSB and STH treatments. Total N loss as a % of N applied for the spring treatments ranged from 11.90 % from the STH treatment to 18.94 % from the SSB. There were no significant differences in total N loss as a % of N applied between any of the spring treatments. There was a significantly greater amount of total N lost as a % of N applied from the spring PL treatment in comparison to the autumn PL treatment ($p<0.05$), there were no other significant differences between spring and autumn treatments.

6.3.4 Indirect N_2O emissions

Indirect N_2O emissions resulting from NH_3 volatilization and nitrate leaching were calculated. The LM treatment had the greatest indirect N_2O emissions following both the autumn and spring applications of 0.94 and 0.88 kg $\text{N}_2\text{O-N}$, respectively. Indirect N_2O emissions from all of the spring treatments except the PL were greater than the direct N_2O emissions. Total direct and indirect N_2O emissions were also calculated. Total N_2O emissions were greater from all of the autumn treatments than the spring with maximum emissions of 3.85 kg $\text{N}_2\text{O-N}$ from the autumn LM compared to maximum emissions of 1.73 kg $\text{N}_2\text{O-N}$ from the spring LM.

6.3.5 Grain yield and yield scaled emissions

Maximum grain yield from the autumn treatments was 3.5 t ha^{-1} from the PL treatment and this was significantly greater ($p < 0.05$) than the minimum grain yield which was obtained from the CON treatment with a value of 2.4 t ha^{-1} (Figure 3a). There were no other significant differences between grain yields from any other treatments. Grain yield from the spring treatments ranged from 1.7 t ha^{-1} for the control treatment to 5.1 t ha^{-1} for the LM treatment (Figure 3a). Grain yield from the LM treatment was significantly greater ($p < 0.05$) than from the control treatment, there were no other significant differences between treatments. There were no significant differences between grain yields from the autumn and spring treatments, except for significantly greater grain yield from the spring LM treatment in comparison to the autumn LM treatment ($p < 0.05$). Grain yields from the autumn and spring treatments were lower than would usually be expected due to delayed crop sowing as a result of unsuitable weather conditions and damage to the growing crop caused by birds.

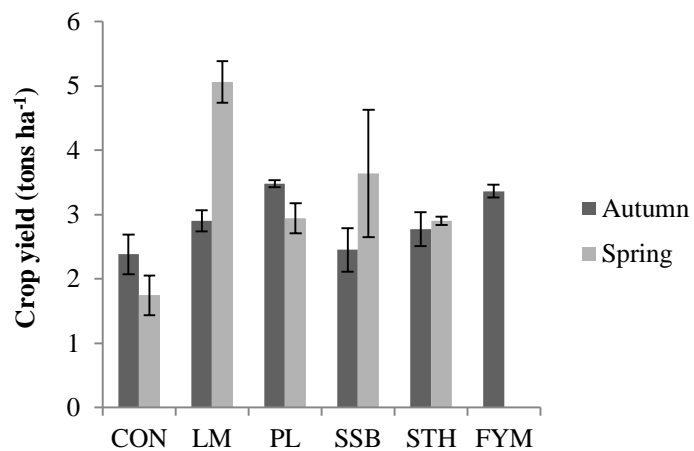
Yield scaled emissions (N_2O and NH_3 emission intensity) from the autumn treatments ranged from $0.3 \text{ kg N}_2\text{O-N} + \text{NH}_3\text{-N ton}^{-1}$ grain for the CON treatment to $14.6 \text{ kg N}_2\text{O-N} + \text{NH}_3\text{-N ton}^{-1}$ grain from the LM treatment (Figure 3b). The yield scaled emissions from the autumn LM were significantly higher than from all other treatments ($p < 0.01$), and the yield scaled emissions from the autumn SSB and STH were significantly higher than from the FYM and CON ($p < 0.01$). Autumn FYM has significantly lower yield scaled emissions than all other autumn treatments except the PL and CON ($p < 0.01$). Yield scaled emissions from the spring treatments ranged from $0.37 \text{ kg N}_2\text{O-N} + \text{NH}_3\text{-N ton}^{-1}$ grain for the CON treatment to $7.42 \text{ kg N}_2\text{O-N} + \text{NH}_3\text{-N ton}^{-1}$ grain from the LM treatment (Figure 3b). There were significantly greater yield scaled emissions from the spring LM and PL compared to all other spring treatments ($p < 0.01$). Yield scaled emissions from the spring PL were significantly greater than from the autumn PL ($p < 0.01$) and yield scaled emissions from the autumn LM were significantly greater than

from the spring LM ($P < 0.01$). There were no other significant differences between autumn and spring treatments.

Grain N uptake from the autumn treatments ranged from 32 kg N ha⁻¹ for the CON treatment to 49 kg N ha⁻¹ from the FYM treatment (Figure 4). There was a significant difference between grain N uptake from the CON and FYM treatments ($p < 0.05$) but there were no other significant differences between treatments. The greatest grain N uptake from the spring treatments was 71 kg N ha⁻¹ from the LM treatment and the lowest grain N uptake was 23 kg N ha⁻¹ from the CON treatment. Grain N uptake from the LM and the SSB treatments was significantly greater than from the CON treatment ($p < 0.05$) and there were no other significant treatment effects. There was significantly greater N uptake from the spring applied LM and SSB treatments in comparison to the autumn applied treatments ($p < 0.05$). There were no other significant differences between the spring and autumn treatments.

Figure 3 a). Harvest 2013 winter wheat grain yields for each treatment. **b).** N_2O and NH_3 emission intensities of crop yield (kg N_2O -N and NH_3 -N per ton of grain)

a).



b).

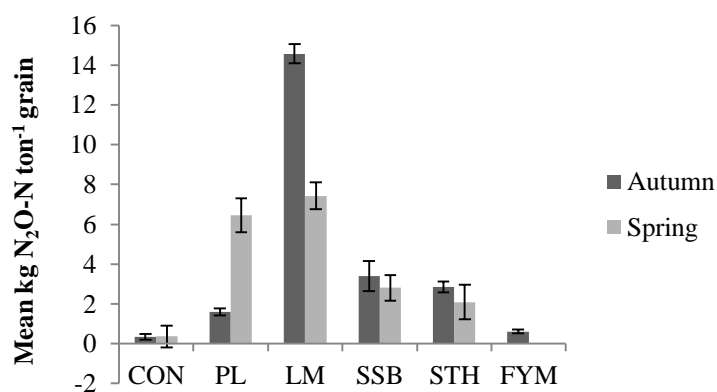
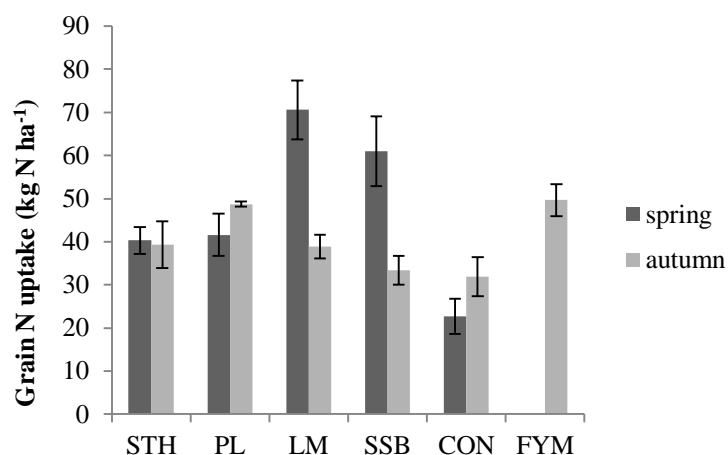


Figure 4. *Winter wheat grain N uptake (kg N ha^{-1}) from the autumn and spring treatments.*

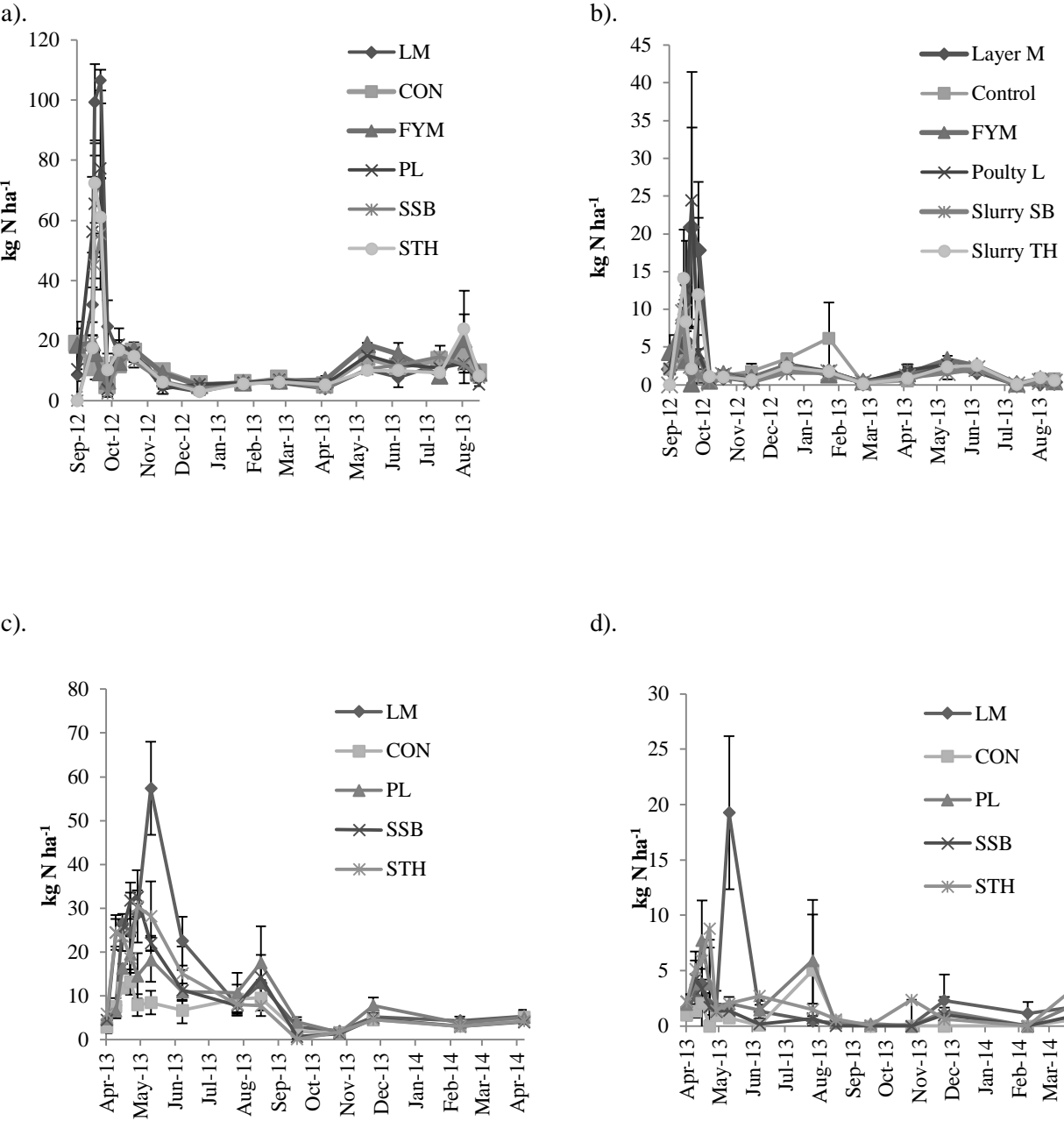


6.3.6 Soil mineral N

Soil NO_3^- -N contents increased rapidly in all treatments following fertiliser application during the autumn experiment (Figure 5a). The largest soil NO_3^- -N content of 107 kg N ha^{-1} was measured from the LM treatment on 10th October 2012 (7 days after fertiliser application). Following peaks in soil NO_3^- -N content from all treatments on either 5th or 10th October 2012, NO_3^- -N concentrations then decreased and remained $<24 \text{ kg N ha}^{-1}$ for the remainder of the experiment. Soil NH_4^+ -N contents from the autumn treatments peaked between 3rd October- 10th October with a maximum NH_4^+ -N content of 24 kg N ha^{-1} from the PL treatment (Figure 5b). Soil NH_4^+ -N contents then decreased to $<3 \text{ kg N ha}^{-1}$ until the end of the experiment, except for a small peak in NH_4^+ -N concentration of 6 kg N ha^{-1} from the CON treatment in February 2013. Soil NO_3^- -N concentrations increased following the spring fertiliser applications, with peaks in all treatments from 12th April to 13th May, and a maximum NO_3^- -N concentration of 57 kg N ha^{-1} from the LM treatment, 33 days after application (Figure 5c). NO_3^- -N concentrations then decreased and from 10th June remained under 23 kg N ha^{-1} for the rest of the experiment. Soil NH_4^+ -N contents increased after spring fertiliser application with peaks occurring

between 12th April to 13th May and a maximum $\text{NH}_4^+\text{-N}$ concentration of 19 kg N ha⁻¹ from the LM treatment 33 days after fertiliser application (Figure 5d).

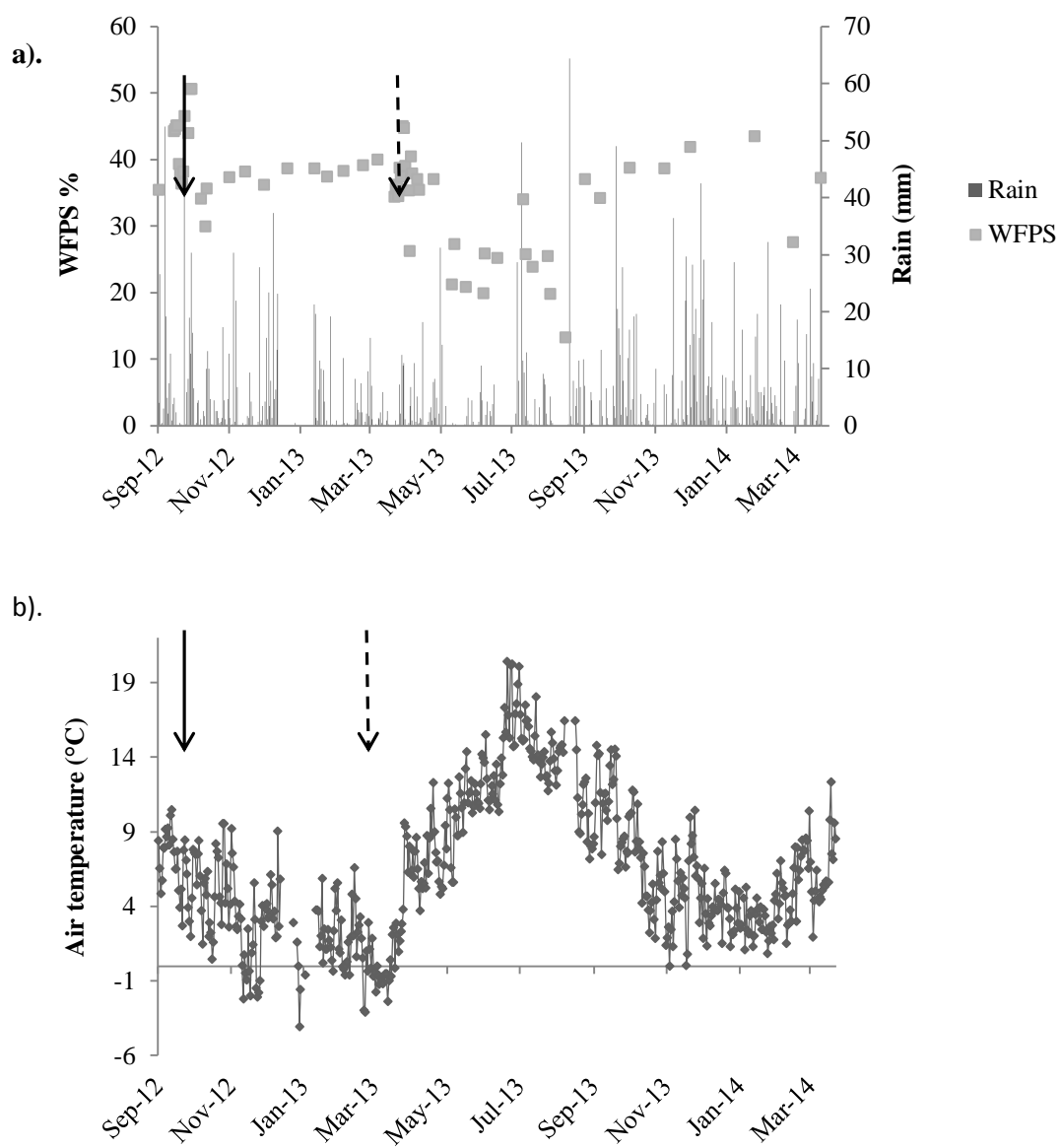
Figure 5. Soil mineral N contents during the experimental period at Boghall. **a)** Autumn NO_3^- and NO_2^- **b).** Autumn NH_4^+ **c).** Spring NO_3^- and NO_2^- **d).** Spring NH_4^+



6.3.7 Environmental conditions

Rainfall occurred frequently throughout the measurement period, with the most frequent and largest events occurring during the autumn and winter periods. The largest daily rainfall event of 55 mm took place in September 2013 (Figure 6a). Total rainfall during the measurement period was 2108 mm. Soil % WFPS was closely related to rainfall, however soil % WFPS remained <60 % for the entire experiment and there was a period of very low % WFPS from the end of April 2013 to the beginning of September 2013, during which time the mean % WFPS was 32 % (Figure 6a). Air temperature throughout the experiment followed seasonal patterns with the highest temperatures occurring during the summer months and lowest during the winter months (Figure 6b). The mean daily January temperatures in 2013 and 2014 were 0.7°C and 3.4°C respectively in comparison to the 40 year mean January temperature of 3.8°C. The mean daily July temperature was 15.8°C in comparison to the 40 year mean July temperature of 13.3°C. There was a considerable difference in the temperatures during autumn and winter 2012 compared to autumn and winter 2013, with higher temperatures during 2013. During winter 2013, mean daily air temperature only fell <0°C once, but during winter 2012 this occurred 38 times.

Figure 6. a). Calculated soil water filled pore space (WFPS) and daily rainfall during the N_2O measurement period. **b).** Mean air temperature during the measurement period. Solid arrow indicates timing of autumn fertiliser application, dashed arrow indicates timing of spring fertiliser application.



6.4. Discussion

6.4.1 Timing of fertiliser application

Nitrous oxide emissions showed considerable temporal variation over the experimental period, with differences evident between emissions from the autumn and spring applications. The large peak in N₂O emissions 9 days after the autumn fertiliser application demonstrates the impact of rainfall and soil WFPS on N₂O production. Soil WFPS was 52 % on the day of autumn fertiliser application, which was already considerably higher than that of 40 % on the day of spring fertiliser application. However, large rainfall events immediately following the autumn application increased soil WFPS to 59 %. This was the highest value recorded during the entire experimental period. The greatest N₂O emissions from soil are expected to occur at WFPS between 50-70 %, with denitrification being the dominant N₂O producing process at > 60 % WFPS (Davidson, 1991; Dobbie et al., 1999), hence the soil WFPS values recorded after the autumn application are likely to have promoted substantial production of N₂O. Soil WFPS has previously been demonstrated to influence N₂O production, particularly in the period immediately following organic fertiliser application when the often large amounts of NH₄⁺ and C in organic fertilisers promote N₂O production by nitrification and denitrification. (Clemens and Huschka, 2001). Soil temperature also influences N₂O emissions, with higher soil temperatures being shown to enhance N₂O production (Smith et al., 2003). The majority of N₂O emissions are thought to occur in the month immediately following fertiliser application (Dobbie et al., 1999), and during this period, the mean soil temperature in the autumn was 9°C and in the spring was 6°C, which suggests that the greater soil temperature in the autumn may also have promoted greater N₂O emissions. The greater cumulative N₂O emissions and N₂O as a % of N applied, from all of the autumn treatments in comparison to the spring is likely to reflect the large peak in emissions during the autumn which occurred immediately following fertiliser application associated with the higher WFPS and temperatures than the spring, and the generally wet winter conditions which were prevalent following the autumn application.

Although the weather conditions during this experiment obviously influenced N₂O emissions they are reflective of the longer term average rainfall and temperature patterns over the last 30 years which demonstrate greater rainfall and higher temperatures in autumn compared to spring in this location (Met Office, 2014). This combined with previous research which has also demonstrated greater N₂O emissions from autumn applied organic fertiliser compared to spring (Thorman et al., 2007), suggests that it is possible to state that generally N₂O emissions are likely to be greater following autumn applications of organic fertiliser in comparison to spring applications. Calculated indirect N₂O emissions showed little variation depending on fertiliser application season. However, they make a considerable contribution to total N₂O emissions which must be taken into account. The relationship between N₂O emissions and soil WFPS and temperature, indicates that N fertiliser should be applied in dry weather conditions if production of N₂O is to be minimised, this will also minimise losses of N via nitrate leaching and is recommended by Defra (2010). The application of manures to agricultural land is already restricted in the autumn in many areas by Nitrate Vulnerable Zone (NVZ) requirements (The Scottish Government, 2014). However, the results of this experiment demonstrate that large emissions of N₂O may still occur even when organic fertilisers are applied outwith the restricted areas and that perhaps the regulations should be more widespread. However, enforcing this could be controversial as the amount of storage areas for organic fertilisers to be kept overwinter would need to be increased to correspond with NVZ rules (FAS, 2013).

Incorporation of the autumn fertiliser applications (except the FYM) may also have promoted N₂O production, by providing rapid access to the fertiliser N by the soil micro-organisms, and by increasing soil moisture. This is in contrast to the spring applications which would have remained on the surface of the soil for longer and would therefore have been more inaccessible to the soil microorganisms, supporting the findings of Wulf et al. (2001), Velthof et al. (2003) and Perala et al. (2006). It has previously been suggested that crop growth may influence emissions as the use of N by the crop will

affect the amount of N remaining in the soil which can potentially be lost from the system (Granli and Bockman, 1994). The sowing of the crop 3 weeks after the autumn fertiliser application meant that during the 3 weeks following application when soil N concentrations were high, there was no demand for N from the crops. The soil N could therefore easily be lost via transformation to N_2O , as was observed, or leaching. However, by the time of the spring application the crop was actively growing and hence greater N uptake was expected as has been demonstrated previously by Limaux et al. (1999). However, except for the LM and SSB treatments there was no significant difference between crop N uptake for the autumn and spring applied treatments and therefore this is unlikely to have influenced the seasonal differences between either N_2O or NH_3 emissions. There was very little difference between the LM NH_3 emissions in the autumn or the spring and this may explain why there was significantly greater crop yield from the spring applied LM than the autumn, as lower N_2O emissions and very similar NH_3 emissions were produced from the spring treatment, potentially allowing an increase in N uptake by the spring treatment crop. The general lack of difference in crop yield between the autumn and spring treatments, combined with generally greater N_2O emissions in the autumn and greater NH_3 emissions in the spring results in similar yield scaled emissions for both autumn and spring for most treatments. It is desirable to achieve low yield scaled emissions as this suggests that the minimum amount of emissions per unit of yield is being obtained. However, the results obtained from this experiment suggest that fertiliser application season has no effect on yield scaled emissions.

Despite the generally greater NH_3 emissions associated with the spring treatments, the only treatment for which there was a significant difference in NH_3 emissions related to application timing was the PL, which had significantly greater emissions in the spring experiment. The spring applied PL had double the amount of readily available N compared to the autumn applied PL which could account for the greater NH_3 emissions from the spring treatment (Defra, 2010). A greater amount of readily available N could

also increase N_2O emissions, but the fact that this did not occur suggests that the readily available N may have been in the form of uric acid. However, uric acid N only accounted for approximately 7 % of the PL readily available N. A more likely explanation for the significantly greater NH_3 emissions from the spring applied PL and the significantly lower N_2O emissions, is that the lack of incorporation of the spring PL reduced availability of the fertiliser N to soil microorganisms as the fertiliser remained on the soil surface for longer. Previous research has also demonstrated decreased NH_3 emissions with rapid incorporation of fertiliser following application (Wulf et al. 2001; Rodhe et al. 2006). Another potential explanation for the higher spring NH_3 emissions could be due to the lower rainfall and soil moisture at the time of the spring fertiliser application in comparison to the autumn, as dry conditions promote NH_3 production (Defra. 2010), however this is in contrast to the findings of Akiyama et al. (2004) who observed no influence of soil water content on NH_3 emissions. Air temperature can also influence NH_3 emissions, with greater emissions during periods of higher temperatures (Meisinger and Jokela, 2000) although the lower temperatures at the time of the spring application compared to the autumn suggests that the dry conditions were more influential than the temperature on the day of application in determining the magnitude of NH_3 emissions. The general trend for lower rainfall during the spring compared to the autumn (Met Office, 2014) suggests that NH_3 emissions are often likely to be greater in the spring as was observed during this experiment.

6.4.2 Type of fertiliser application

The effect of the type of fertiliser on N_2O emissions was dependent on the season of fertiliser application; this suggests that weather conditions are very influential in determining N_2O emissions. The high N_2O emissions from the autumn slurry treatments are suggested to be due to the low dry matter (and therefore high moisture) contents of the slurry (2 % compared to 18-42 % for the other autumn applied treatments) which may have increased soil moisture content and N_2O production by denitrification. This

can occur immediately following slurry application (Davidson, 1992). Although measured soil WFPS remained below the denitrification “threshold” of 60 %, it is assumed that the slurry application would have caused localised increases in soil WFPS that were > 60 %. The measured soil WFPS values are the mean of mixed samples taken from random plots and are therefore unlikely to represent the high soil moisture content associated with slurry application. The extremely high C:N ratio of the slurry treatments may also have influenced production of N₂O due to growth of microbial biomass and their subsequent oxidation of the decomposable carbon which would have produced localised areas of anoxic soil and enhanced denitrification (Akiyama et al., 2004; Clemens and Huschka, 2001; Pierzynski, 2005). The differences in N₂O emissions seen between the autumn treatments were not observed following the spring applications. The effect of low rainfall and low soil temperatures at the time of spring fertiliser application may account for the small N₂O emissions and the negligible differences between emissions at this time.

The timescale over which NH₃ emissions occurred varied between treatments, with higher and longer lasting emissions from the LM and PL compared to other treatments. This is suggested to be due to the large application rates and high NH₄⁺-N contents of these treatments which promote NH₃ production after fertiliser application, in addition to their high dry matter contents. Organic fertilisers with high dry matter contents such as PL and LM have previously been demonstrated to cause longer lasting NH₃ emissions following application than treatments with high moisture contents such as slurries due to faster infiltration of slurry into the soil (Chambers et al., 1999; Menzi et al., 1997). Ammonia emissions from the slurry treatments during 24 hours following application had a mean value of 52 % of total slurry NH₃ emissions. This supports previous work where liquid slurry was observed to lose between 50- 90 % of its total NH₃ emissions in the first 24 hours following application due to increases in slurry pH due to urea hydrolysis and ammoniacal N concentration due to loss of slurry moisture following application (Meisinger and Jokela, 2000).

The high $\text{NH}_4^+\text{-N}$ content of the LM is also associated with the significantly greater grain yield from the spring LM in comparison to the control. The significantly greater N uptake of the spring LM compared to other treatments will have promoted greater crop growth. The lack of significant differences in crop yield between all of the autumn treatments and the N uptake of the grain, despite differences in the amount of N applied for each treatment, reflects the differences in loss of N as N_2O and NH_3 , and also potential differences in losses of N via leaching are not accounted for.

Yield scaled emission calculations for the autumn treatments suggest that the FYM or PL are the optimum treatments if N_2O and NH_3 emissions are to be minimised whilst crop yield remains high as these treatments have significantly lower yield scaled emissions than the others. The lower yield scaled emissions of the spring applied SSB and STH suggest that these treatments are the optimum treatments to apply in the spring if crop yield is to be maintained but emissions of NH_3 and N_2O are to be reduced. However, the spring STH and SSB treatments did not produce significantly greater yield than the CON treatment and there was also no significant difference in N_2O or NH_3 between these treatments. This suggests that there is no obvious benefit to the yield scaled emissions of applying any organic fertiliser, and hence no environmental or economic benefits. It is therefore more financially beneficial to apply no fertiliser due to the costs saved in obtaining and applying the fertiliser. The difference between the optimum fertiliser to apply based on yield scaled emissions during the autumn and the spring draws attention to the need to consider the timing of fertiliser application when choosing the most appropriate fertiliser. It can however be stated that the LM treatment was the most inappropriate treatment in both the autumn and the spring due to its high yield scaled emissions following both applications.

6.4.3 Method of fertiliser application

The results demonstrated that the method of slurry application had no effect on either N_2O or NH_3 emissions which may be linked to the lack of effect also observed on crop yield or yield scaled emissions. Previous research has demonstrated 30-70 % lower NH_3 emissions from bandspread slurry in comparison to surface broadcast slurry (Pain and Misselbrook, 1997; Webb et al. 2010) in contrast to the results demonstrated from this research. Although the slurry treatments were applied using different methods, they generally remained on the soil surface for the same amount of time. The autumn treatments both underwent incorporation at the same time but neither of the spring treatments were incorporated. The actual method of slurry application has been found to only account for <1 % of total NH_3 emissions (Meisinger and Jokela, 2000) hence if the action of the slurry once it is on the ground is similar following either application method, then NH_3 emissions are also likely to be similar. Although there was no significant effect of fertiliser application method on N_2O or NH_3 emissions, slurry incorporation does appear to be effective at decreasing NH_3 emissions, although it increased N_2O emissions, supporting the findings of Perala et al. (2006), Velthof et al. (2003), Wulf et al. (2001).

6.4.4 Comparison to previously reported EFs and the IPCC default EF

There was considerable variation in the N_2O and NH_3 EFs obtained from different treatments and different application times. This variation in EFs from soil amended with organic fertilisers is also evident in previous research. Our research produced mean N_2O EFs from SSB of 2.69 and -1.10 % from the autumn and spring treatments, respectively, demonstrating considerable variation in EFs within treatments. However, this range has also been reported by previous work which has produced N_2O EFs for SSB treatments of 0.97 %, 0.12 % (Chadwick et al., 2000) and 0.4 % (Velthof et al., 1992). The N_2O EF for LM of 2.4 % found by Webb et al. (2014) is within the range found in our experiment of 0.86- 0.18 % (autumn and spring applications respectively). The autumn

and spring N₂O EFs of 0.81 % and 0.34 % respectively, from the PL and 0.31 % from the autumn FYM as shown by our work are greater than those of 0.05 % for PL (Chadwick et al., 2000) and 0.33 % and 0.22 % from FYM (Webb et al., 2014). NH₃ EFs from our research and from the literature are also highly variable. Previous research has determined NH₃ EFs for surface spreading of cattle slurry of 6-12 % (Van der Hoek, 1998), in comparison to our mean values of 8.53- 19.18 %. EFs for LM have previously been reported to range from 0.15 % (Van der Hoek, 1998) to 7 % (Sommer and Hutchings, 2001) compared to a greater value of 16 % from this research. The EF obtained for PL by Sommer and Hutchings (2001) is within the range obtained in our experiment of 2.56-14.75 %. The range in N₂O and NH₃ EFs as demonstrated by this experiment and previous work, reveals the effect of factors such as soil type, soil conditions and manure properties on emissions. The need for EFs which take into account the type of fertiliser used is also highlighted by the variation in EFs between fertiliser types, particularly between solid and liquid manures as solid manures such as FYM often produce lower N₂O and NH₃ emissions and EFs due to their smaller available N content (Chadwick et al., 2011).

The variation between the autumn and spring N₂O EFs from this experiment make it difficult to assess the appropriateness of the IPCC's default 1.25 % EF. The mean autumn EF of 1.49 % is reasonably similar to the IPCC EF of 1.25 % and does not support the UK's movement to the 1 % EF in the near future. However, the spring N₂O EF of -0.33 % is much lower than both of the IPCC's EFs. The overall mean (autumn and spring treatments combined) N₂O EF of 0.68 % indicates that the new IPCC EF of 1 % overestimates N₂O emissions as a proportion of N applied. The main findings of this research with regards to N₂O EFs are that the type of organic fertiliser used influences the N₂O EF, but that the timing of fertiliser application is also important with regards to EFs. This research has also demonstrated that often the weather conditions following autumn fertiliser and spring fertiliser application will be markedly different and this makes the use of a single EF for all fertilisers and all application timings inappropriate.

All of the NH_3 EFs calculated for the autumn and spring treatments were lower than the IPCC's default NH_3 EF of 20 %. The mean spring EF of 15.5 % is closer to the IPCC's EF than the mean autumn EF of 7.3 %, however, the overall mean NH_3 EF of 10.9 % is much lower than the IPCC's default. The low NH_3 EFs from both the autumn and the spring treatments, despite the different weather conditions experienced during these times, indicates that the IPCC's EF overestimates the amount of NH_3 emitted from organic fertiliser. However, it may be that another property of the experimental site, such as the soil type or pH, is influencing the amount of NH_3 emitted, and therefore further research into NH_3 emissions from organic fertiliser applications in different locations across the UK is required.

6.5. Conclusion

The results of this research demonstrate the influence of organic fertiliser type and application timing on N_2O and NH_3 emissions. Emissions of N_2O and NH_3 were strongly affected by the season of fertiliser application, reflecting the effects of weather conditions, crop growth and fertiliser incorporation on production of N_2O and NH_3 . Fertiliser type was influential in determining the magnitude of N_2O and NH_3 emissions, demonstrating the effects of fertiliser properties such as moisture content and available N content. The use of different methods for applying the slurry treatments had no effect on N_2O or NH_3 emissions and also did not influence crop yield or yield scaled emissions. Crop yield was generally unaffected by fertiliser application season or fertiliser type, however, yield scaled emissions were shown to be influenced by fertiliser application season, with the treatments producing the lowest yield scaled emissions varying between the autumn and spring applications. There was high variability in N_2O and NH_3 EFs dependent on fertiliser type and application season. The variability of N_2O and NH_3 EFs means that there is also considerable deviation from the IPCC's standard N_2O and NH_3 EFs. This highlights the need for N_2O and NH_3 EFs which take into account the effect of different fertiliser types and application seasons on emissions, in order to improve the accuracy of the UK's agricultural N_2O and NH_3 inventory. Trade-offs between N_2O and NH_3 emissions when mitigation strategies such as incorporation of fertilisers takes place must be carefully considered. Future research is needed to determine whether the results obtained from this work are applicable to different geographical areas, and also to take into account the loss of N via leaching.

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Chapter 7.

Evaluation of ammonium and nitrate retention by six biochars using a batch sorption experiment

Evaluation of ammonium and nitrate retention by six biochars using a batch sorption experiment

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Abstract

The amendment of agricultural soils with biochar and the possible subsequent retention of NH_4^+ and NO_3^- by the biochar has been suggested as a means by which N_2O emissions from soils may be decreased. This experiment tested the affinity and capacity for NH_4^+ and NO_3^- of six biochars made from miscanthus straw (at 2 pyrolysis temperatures), oil seed rape straw, willow, mixed softwood and mixed hardwood feedstocks at pyrolysis temperatures between 450-550°C using a batch sorption experiment. The effect of biochar particle size on NH_4^+ and NO_3^- retention was investigated by using two particle sizes of biochar, these were <1 mm and 1-4 mm. The biochar was sterilised before use by autoclaving. Biochar properties including moisture content, pH, C and N contents were measured. The biochars were mixed with NH_4NO_3 solution at concentrations of 0, 25, 50, 75, 100 and 500 mg $\text{NH}_4\text{NO}_3 \text{ L}^{-1}$ (referred to as exposure levels 1-6) and the equilibrium adsorption data was described using the initial mass isotherm approach. All the biochars demonstrated affinity for NH_4^+ and NO_3^- with maximum removal of 32 % of NH_4^+ and 11 % of NO_3^- respectively by miscanthus straw biochar (pyrolysis temperature 500°C). There was greater release of NO_3^- than NH_4^+ from all biochars. There was a significant negative relationship between biochar particle size and NH_4^+ retention but no effect on NO_3^- retention. Biochar particle size and pH did not influence NH_4^+ and NO_3^- sorption. The results of this experiment demonstrate the

potential for biochars of different feedstocks to retain N and suggest that this may influence N₂O emissions in biochar amended soils.

7.1 Introduction

The application of biochar to soils has been shown to have numerous environmental benefits and has recently gained interest due to its potential to act as a sorbent for nutrients or contaminants in soil (Ahmad et al., 2014). Biochar is the carbon rich product resulting from the pyrolysis of a range of materials including waste sources such as crop residues, woody materials and manures (Lehmann and Joseph, 2009). Biochar is very stable in soil due to its composition of carbon (C) in a highly recalcitrant chemical form (Shackley and Sohi, 2010), resulting in the ability of soils amended with biochar to sequester C for timescales up to thousands of years (Fowles, 2007). Biochar also has a large surface area and predominantly negative surface charge, giving it the ability to retain ions from the soil or solution (Ding et al., 2010). In addition to the benefits associated with increased C storage and a subsequent reduction in loss of C to the atmosphere, research suggests that biochar may improve the soil ecosystem through numerous means. Biochar has the ability to retain nutrients and to improve aspects of soil physics and biology such as soil structure, aeration and water holding capacity (Johnson et al., 2007; Lehmann et al., 2006), all of which may result in enhanced soil fertility and increased crop yield (Koide et al., 2011). Recent research has indicated that biochars produced from a range of feedstock sources and pyrolysis production temperatures, have the ability to reduce N₂O emissions from agricultural soils (Case et al., 2012; Rogovska et al., 2011; Spokas et al., 2009; Yanai et al., 2007).

Despite evidence supporting the decrease in N₂O emissions from biochar amended soils, the mechanisms responsible for this process are relatively poorly understood. The operation of numerous mechanisms has been suggested, with three of these gaining particular research interest. Firstly, research has suggested that biochar is able to retain NH₄⁺ and NO₃⁻, which are the substrates required for the production of N₂O by nitrification and denitrification. Biochar has a high cation exchange capacity (CEC) and therefore the potential to retain cations such as NH₄⁺ (Shenbavgalli and Mahimairaja,

2012). This causes a decrease in the N_2O producing capacity of the soil as excess NH_4^+ will be bound to biochar and be less available for conversion to N_2O by nitrification (Clough and Condron, 2010). Biochar properties such as pH and pyrolysis temperature have been suggested to affect the CEC, with an increase in CEC occurring with an increase in biochar pH and a decrease in CEC with increasing pyrolysis temperature (Hollister, 2013). A variety of mechanisms have been suggested to account for NO_3^- sorption by biochar. Prendergast-Miller (2011) suggested that physical retention of NO_3^- in solution in biochar pores was occurring after observing NO_3^- sorption, and that this decreased N_2O production by denitrification. Kameyama et al. (2012) observed NO_3^- sorption and suggested that this is due to anion exchange, with anion exchange capacity (AEC) increasing with increasing pyrolysis temperature. This is based on an increase in biochar ash content at higher temperatures which causes an increase in biochar pH due to the formation of basic functional groups which can adsorb NO_3^- . This has been challenged by Cheng et al. (2008) who suggest that decreasing biochar pH would lead to an increase in surface positive charge resulting in adsorption of anions such as NO_3^- . Bridge bonding of NO_3^- has been suggested by Mukherjee et al (2011) as another mechanism by which biochar may adsorb NO_3^- , this involves the use of residual charges of divalent cations or metals including Ca_2^+ and Al_3^+ to bond NO_3^- to the biochar.

The second mechanism proposed by which biochar may reduce N_2O emissions is through alteration of soil structure caused by biochar addition which improves soil aeration. This acts to reduce denitrification which occurs under anaerobic conditions in poorly aerated soil (Clough and Condron, 2010). However recent research by Case et al. (2012) using hardwood biochar applied to soil from a miscanthus plantation suggests that the soil aeration mechanism may only have minimal impact on N_2O emissions with immobilisation of NO_3^- mainly responsible for reducing N_2O emissions. The third mechanism relates to the high pH of biochar associated with its large ash content. After application to soil, this results in an increase in soil pH which affects soil N_2O production and consumption since nitrifiers perform well in slightly acidic to slightly

alkaline pH soils whereas denitrifiers perform well within the soil pH range 4-8. Biochar-induced increases in soil pH were found to cause a shift in the $\text{N}_2\text{O}:\text{N}_2$ ratio as N_2O is preferentially converted to N_2 (Clough and Condron, 2010). Yanai et al. (2007), however, demonstrated that the alkalinity of biochar is not the only mechanism responsible for reduction of N_2O emissions, and that it may be working simultaneously with improved soil aeration to decrease N_2O emissions.

Despite the lack of understanding surrounding the means by which biochar reduces N loss from soils, few studies have investigated the exact mechanisms responsible for it; this is necessary if biochar is to be used successfully as a soil amendment to reduce environmental impacts such as leaching and N_2O emissions. This would then enable prediction of the magnitude of mitigation associated with particular biochars, informing decisions about appropriate biochar application rates to maximise reductions in N loss. This study focuses on NH_4^+ and NO_3^- retention capabilities of biochar with the purpose of determining the affinity of different biochars for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ and subsequently whether there is a variation in capacity of different biochars to retain N and the biochar properties responsible for this. The effect of biochar particle size on N retention is assessed through the use of two different particle sizes. These aims are achieved through the use of batch sorption experiments using 6 carefully selected and characterised biochars from different feedstock sources and pyrolysis temperatures.

7.2. Materials and methods

7.2.1 Biochar selection and preparation

Biochar was obtained from the UK Biochar Research Centre, Edinburgh (UKBRC) and BTG (Shell Research Ltd). Six types of biochar were selected and feedstocks consisted of a range of straw and wood waste products with slow pyrolysis temperatures ranging between 450- 550°C (Table 1). The biochar was sieved to obtain two uniform particle size ranges: <1.00 mm and 1-4 mm. To eliminate any microbial influences and ensure that the biochar was sterile before the batch sorption experiment commenced, biochar was moistened and autoclaved for two cycles of 30 minutes at 121°C (more details of this procedure are described in Appendix 3). The biochar was then oven dried at 40°C for 24 hours. Biochar C and N analysis was carried out using a Carlo Erba NA 2500 Elemental Analyser. pH and moisture analysis was carried out following the methods of Angst et al. (2013a).

Table 1. *Biochar properties*

Biochar feedstock	Production facility	Pyrolysis temp (°C)	C content %	N content %	pH	Moisture %
Miscanthus straw (a)	UKBRC	500	65.73	0.43	6.27	4.42
Miscanthus straw (b)	BTG	450	70.69	0.40	6.66	6.39
Oil seed rape straw (c)	UKBRC	550	67.84	0.30	8.44	4.12
Willow (d)	UKBRC	550	84.24	0.67	7.64	2.80
Mixed hardwood (e)	UKRBC	550	95.18	0.08	6.90	16.62
Mixed soft wood (f)	UKBRC	550	84.48	0.06	6.50	3.10

7.2.2 Batch sorption experiment

Two batch sorption experiments were carried out to measure firstly the affinity of the six biochars for NH_4^+ and NO_3^- (experiment a), and secondly the capacity of these biochars to adsorb NH_4^+ and NO_3^- (experiment b). The first experiment used ammonium nitrate (NH_4NO_3) solutions at concentrations of: 0, 25, 50, 75, 100 $\text{mg NH}_4\text{NO}_3 \text{ L}^{-1}$ (referred to as exposure levels 1,2,3,4 and 5 respectively) to which biochar was added at a solid-to-liquid ratio of 1:150. Concentrations of N in mg N L^{-1} at each exposure level were 0, 8.75, 17.50, 26.25 and 35.00 respectively. The second experiment used NH_4NO_3 solution at a concentration of 500 $\text{mg NH}_4\text{NO}_3 \text{ L}^{-1}$, also referred to as 175 mg N L^{-1} (exposure level 6). Experiments were performed in triplicate for each concentration treatment, for each biochar particle size (either <1 mm, or 1-4 mm). The pH of all samples were adjusted to between pH 6-7 using HCl and NaOH to remove any effects of variation in pH between biochars on N retention. Samples were shaken in the dark on an orbital shaker for 16 hours until adsorption equilibrium was reached and the pH of all samples was then recorded. The samples were then centrifuged for 30 minutes at 4300 rpm and filtered through 0.45 micron cellulose nitrate filter paper to remove biochar from the suspension. The aqueous samples were analysed for NO_3^- and NH_4^+ content using a Skalar San⁺⁺ continuous flow autoanalyser (Skalar, York, UK).

7.2.3 Analysis of equilibrium adsorption data

Although Langmuir and Freundlich models are often used to describe equilibrium adsorption data, it was noted in this study that all of the biochars released NH_4^+ and NO_3^- into the aqueous solution, making the Initial Mass Isotherm approach developed by Nodvin et al. (1986), more appropriate to use. Nodvin et al. (1986) developed the Initial Mass Isotherm approach to define the removal or release of anions or DOC by forest soils from an aqueous solution. The Initial Mass Isotherm approach allows for two sources to contribute the analyte of interest to the system, in this case, both the biochar and the aqueous solution of NH_4NO_3 were contributing NH_4^+ and NO_3^- , in addition to

the removal of NH_4^+ and NO_3^- by the biochar. The Initial Mass Isotherm approach involves plotting the amount of solute removed or released (RE) as a function of the initial solute concentration (C_i), this results in linear relationships which can be defined by the equation:

$$\text{RE} = mC_i - b$$

Where m and b represent the values of the slope and the negative intercept of the initial mass isotherm respectively.

Plotting of Initial Mass Isotherms for all biochars over the range of NH_4NO_3 concentrations allowed for comparison of the slope and intercept values which relate to differences between removal (positive values) and release (negative values) of NH_4^+ and NO_3^- by different biochars.

7.2.4 Statistical analysis

Statistical analysis of the results was carried out using Minitab 16. Statistical significance was determined using the 0.05 confidence interval. Regression analysis was used to test for relationships between NO_3^- or NH_4^+ sorption and temperature, and NO_3^- or NH_4^+ sorption and pH. One way analysis of variance (ANOVA) was used to test for differences between NO_3^- or NH_4^+ sorption depending on biochar particle size.

7.3. Results

7.3.1 Biochar affinity for NH_4^+ and NO_3^- (Experiment a)

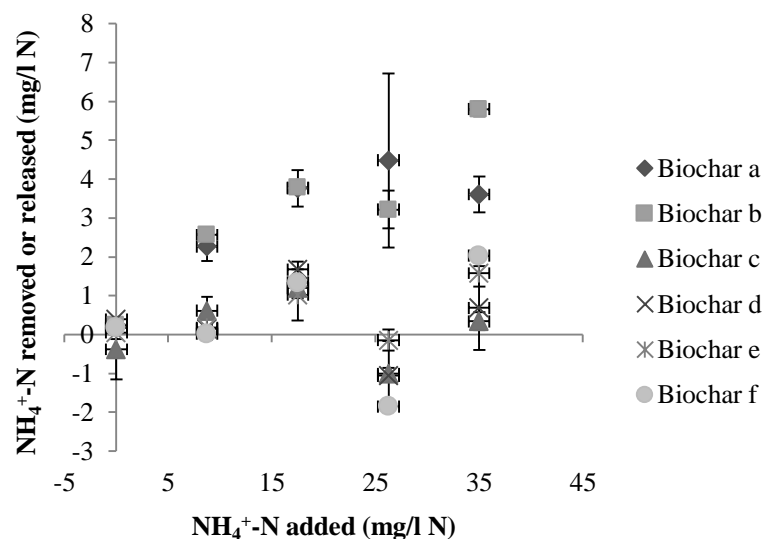
Initial mass isotherms of the adsorption data demonstrate that all the biochars tested, at both particle sizes, showed affinity for NH_4^+ and the ability to remove it from solution (Figure 1a). Linear increases in NH_4^+ adsorption were evident with increasing solution concentration for some biochars, in particular biochars a and b 1-4 mm particle size, and biochar b 1 mm particle size, with a maximum r^2 value of 0.85 obtained for 1-4 mm biochar b (Figure 1a and 1c). Biochars a and b at both particle sizes showed greater affinity for NH_4^+ than biochars c, d, e and f with the maximum quantity of NH_4^+ adsorbed of 5.81 mg N/l by biochar b 1-4 mm size, which was 12 % of the NH_4^+ added in solution (Tables 2a and 2b). The maximum amount of initial NH_4^+ adsorbed by biochars c, d, e and f at both particle sizes was <50 % of that adsorbed by biochars a and b. The % of NH_4^+ added in solution which was removed by the biochars generally decreased as the amount of NH_4^+ added increased (Tables 2a and 2b). The maximum % NH_4^+ removed was 32 % of the NH_4^+ added by biochar a < 1mm at exposure level 1, this decreased to 8 % at exposure level 4. Release of NH_4^+ by the biochar was demonstrated by biochars c, d, e and f at both particle sizes with maximum release of 2.13 mg N/l by biochar f <1mm size, at exposure level 3 (Tables 2a and 2b). This suggests that biochars a and b did not release NH_4^+ , or that removal of NH_4^+ from solution exceeded release. There was no significant difference between NH_4^+ adsorption by <1mm biochar and 1-4 mm biochar ($p>0.05$) for all six biochars studied.

Retention of NO_3^- at all exposure levels was considerably lower than retention of NH_4^+ and release of the sorbate occurred more frequently, however, all biochars displayed affinity for NO_3^- and the ability to remove it from the added solution (Figures 1b and 1d). There was little variation in affinity for NO_3^- between different biochars at either particle size and the maximum NO_3^- adsorbed was 2.79 mg N/l by 1-4 mm biochar f at exposure level 4 which was 8 % of NO_3^- added (Tables 2a and 2b). There was no linear increase in NO_3^- removal related to an increase in solution NO_3^- concentration. Release

of NO_3^- was demonstrated by all biochars with a maximum release of 3.86 mg N/l by biochar b <1 mm at exposure level 4. The % of the added NO_3^- which was removed by the biochar generally decreased with increasing solution concentration from a maximum of 16 % NO_3^- adsorbed by 1-4 mm biochar f at exposure level 2, which decreased to 8 % at exposure level 5 (Tables 2a and 2b). There was no significant difference between NO_3^- adsorption by <1 mm biochar and 1-4 mm biochar, except for biochars a and f size 1-4 mm which adsorbed significantly more NO_3^- than <1 mm at treatment level 3.

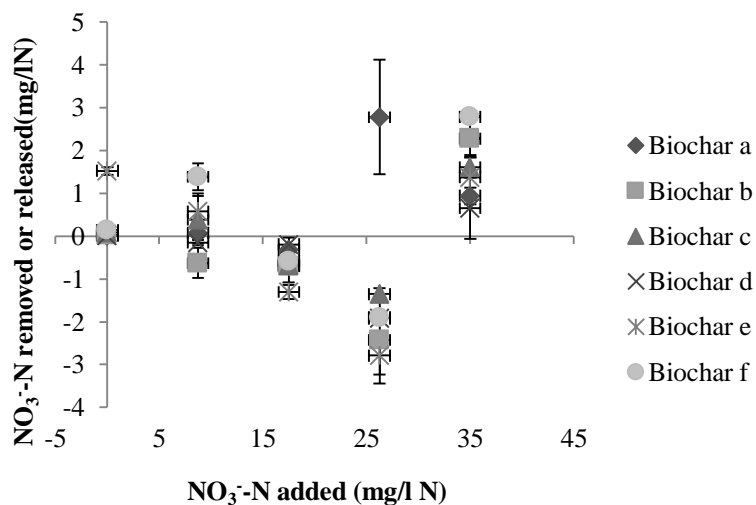
Figure 1. Biochar initial mass isotherms and tables of linear regression equations and R^2 values. **a).** 1-4mm biochar $\text{NH}_4^+\text{-N}$ initial mass isotherms and table **b).** 1-4mm biochar $\text{NO}_3^-\text{-N}$ initial mass isotherms and table **c).** <1mm biochar $\text{NH}_4^+\text{-N}$ initial mass isotherms and table **d).** <1mm biochar $\text{NO}_3^-\text{-N}$ initial mass isotherms and tables.

a).



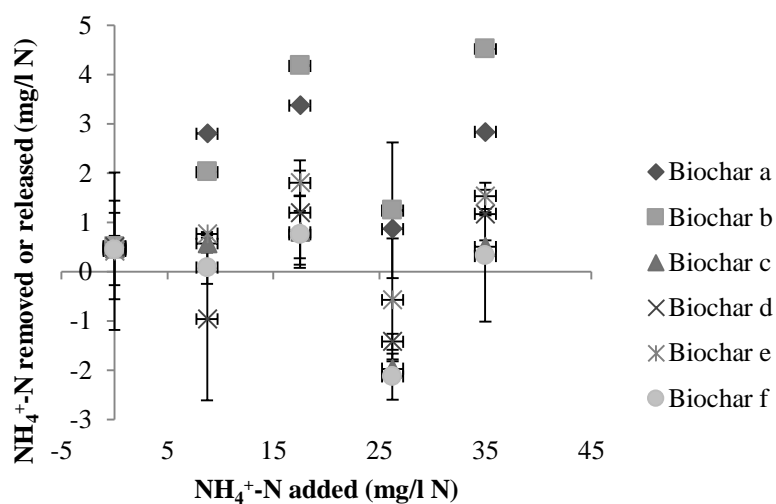
Biochar	Linear regression equation	R^2 value
a	$Y=0.10x + 1.05$	0.71
b	$Y= 0.13x + 0.77$	0.85
c	$Y= 0.0021x + 0.19$	0.0011
d	$Y= 0.007x + 0.49$	0.0095
e	$Y= 0.031x - 0.012$	0.35
f	$Y= 0.021x - 0.020$	0.038

b).



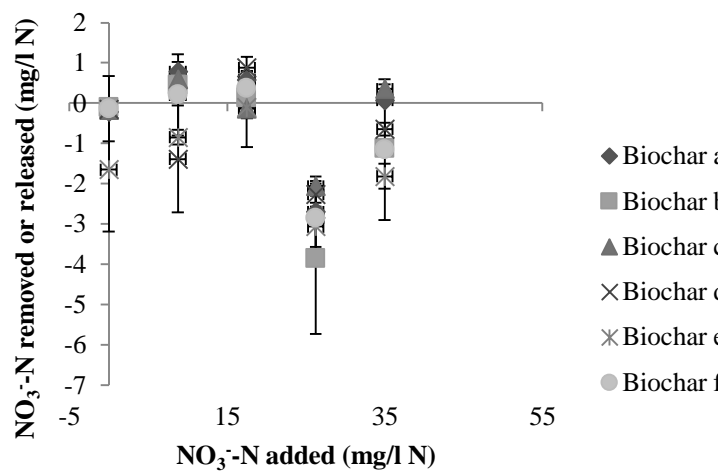
Biochar	Linear regression equation	R ² value
a	$Y = 0.052x - 0.21$	0.33
b	$Y = 0.031x - 0.83$	0.064
c	$Y = 0.015x - 0.25$	0.034
d	$Y = 0.0056x - 0.22$	0.0066
e	$Y = -0.042x + 0.61$	0.097
f	$Y = 0.023x - 0.031$	0.031

c).



Biochar	Linear regression equation	R ² value
a	$Y = 0.032x + 1.52$	0.011
b	$Y = 0.083x + 1.045$	0.41
c	$Y = -0.028x + 0.57$	0.011
d	$Y = 0.0098x - 0.073$	0.012
e	$Y = 0.010x + 0.61$	0.023
f	$Y = 0.028x + 0.38$	0.11

d).



Biochar	Linear regression equation	R^2 value
a	$Y = -0.033x + 0.20$	0.11
b	$Y = -0.072x + 0.37$	0.32
c	$Y = -0.018x + 0.039$	0.060
d	$Y = 0.021x - 0.34$	0.061
e	$Y = -0.029x - 0.99$	0.13
f	$Y = -0.058x + 0.31$	0.36

7.3.2 Biochar capacity to retain NH_4^+ -N and NO_3^- N (Experiment b)

The results of experiment b demonstrate whether biochar has the capacity to adsorb NH_4^+ from a solution with a high concentration of NH_4^+ . All of the biochars removed NH_4^+ from the high concentration solution except <1mm biochar f, with maximum removal of 17 mg/l N by 1-4 mm biochar b (Table 3). Although the biochars displayed the ability to remove NH_4^+ from solution, the capacity for removal at high solution concentrations appears limited as a mean % NH_4^+ removal at exposure level 6 was 4 % and 2 % of the added NH_4^+ for 1-4 mm and <1 mm biochar, respectively, in comparison to mean values of 11 % and 14 % for 1-4 mm and <1 mm biochar, respectively at exposure level 2 (Tables 2a and 2b). There was no significant difference between NH_4^+ sorption at this high concentration depending on the size of the biochar ($p>0.05$).

All of the 1-4 mm biochars removed NO_3^- from the high concentration solution, however only biochar c from the <1 mm biochar category removed NO_3^- (Table 3). The maximum removal was 19 mg N /l by 1-4 mm biochar c. The mean % of the added NO_3^- removed by 1-4 mm biochar was 7 % at exposure level 6, this value was the same as at exposure level 1. However, for individual biochars there was generally a decrease in % NO_3^- removed for exposure level 6 in comparison to lower exposure levels, suggesting that the capacity for NO_3^- removal at high solution concentrations is limited (Tables 2a and 2b). There was no significant difference between sorption of NO_3^- at this high concentration by biochar size 1-4 mm and biochar size >1 mm ($p>0.05$).

Table 2. Percentage of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ sorbate adsorbed by each biochar at exposure levels 2-6 (25, 50, 75, 100, 500 mg $\text{NH}_4\text{NO}_3 \text{ L}^{-1}$) for a). <1mm biochar and b). 1-4mm biochar.

a).

	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed
Exposure level	Biochar a	Biochar a	Biochar b	Biochar b	Biochar c	Biochar c	Biochar d	Biochar d	Biochar e	Biochar e	Biochar f	Biochar f
2	32.04	8.91	23.12	5.22	6.51	6.86	*	*	8.80	*	0.91	2.40
3	19.29	3.31	23.89	0.74	4.57	*	6.86	5.03	10.29	*	4.30	2.13
4	3.29	*	4.74	*	*	*	*	*	*	*	*	*
5	8.10	0.2	12.91	*	1.44	1.01	3.34	*	4.39	*	0.91	*
6	0.29	*	5.35	*	1.24	2.61	1.24	*	0.21	*	*	*

*= $\text{NH}_4^+\text{-N}$ or $\text{NO}_3^-\text{-N}$ released from biochar

b).

	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed	$\text{NH}_4^+\text{-N}$ % adsorbed	$\text{NO}_3^-\text{-N}$ % adsorbed
Exposure level	Biochar a	Biochar a	Biochar b	Biochar b	Biochar c	Biochar c	Biochar d	Biochar d	Biochar e	Biochar e	Biochar f	Biochar f
2	25.91	0.87	29.35	*	6.99	4.42	1.61	*	1.99	6.59	0.27	15.86
3	21.52	*	21.61	*	6.83	*	9.58	*	5.86	*	7.66	*
4	17.09	10.59	12.25	*	*	*	*	*	*	*	*	*
5	10.30	2.69	16.59	6.52	0.98	4.61	1.96	1.87	4.52	3.92	5.79	7.96
6	5.32	1.45	9.79	4.51	3.31	10.85	4.50	8.17	1.92	8.19	0.052	9.14

*= $\text{NH}_4^+\text{-N}$ or $\text{NO}_3^-\text{-N}$ released from biochar

Table 3. <1mm and 1-4mm biochar. NH_4^+ -N and NO_3^- -N adsorption at exposure level 6 (500 mg NH_4NO_3 L^{-1}).

	1-4mm biochar	<1mm biochar	1-4mm biochar	<1mm biochar
Biochar	NH_4^+ -N adsorbed (mg N L^{-1})		NO_3^- -N adsorbed (mg N L^{-1})	
a	9.31	0.50	2.54	-6.37
b	17.14	9.37	7.90	-5.04
c	5.79	2.17	18.99	4.56
d	7.87	2.17	14.30	-0.44
e	3.36	0.37	14.32	-4.04
f	0.09	-1.17	15.99	-2.24

7.4. Discussion

7.4.1 Variation in affinity and capacity of biochars to retain NH_4^+ and NO_3^-

7.4.1.1 Effect of biochar pH and pyrolysis temperature

Variations in the affinity of the different biochars for NH_4^+ and NO_3^- were evident and were observed to vary depending on pyrolysis temperature. CEC has been suggested to be responsible for NH_4^+ sorption by biochar and previous studies have demonstrated that CEC decreases as pyrolysis temperature increases due to carboxyl functional groups being lost during pyrolysis (Cheng et al., 2006; Nguyen and Lehmann, 2009). It would therefore be expected that biochars which are produced at a lower pyrolysis temperature would show a greater ability to sorb NH_4^+ , as demonstrated by Hollister (2013). Zheng et al. (2010) suggested that this relationship between pyrolysis temperature and NH_4^+ sorption only occurred at pyrolysis temperatures of 350- 550°C, and at temperatures <350°C NH_4^+ sorption increased as pyrolysis temperature increased. Pyrolysis temperature also influences the surface area of biochar with high pyrolysis temperatures corresponding to larger surface areas (Mukerjee et al., 2011; Yao et al., 2012), in contrast to the effect of CEC decreasing at higher pyrolysis temperatures. It may be expected that a larger surface area would increase sorption of NH_4^+ . Biochar b (miscanthus straw, 450°C) has the greatest NH_4^+ sorption capacity of all the biochars tested, as shown by its retention of 5 and 10% of the sorbate added at exposure level 6 by the < 1mm and 1-4 mm sizes respectively. The biochar with the smallest sorption capacity (biochar e) had a pyrolysis temperature of 550°C. Regression analysis to test to the relationship between the capacity of the biochars to retain NH_4^+ and the biochar pyrolysis temperature demonstrated a significant negative relationship between these variables for both particle sizes of biochar ($p < 0.05$) with a decrease in NH_4^+ retention as pyrolysis temperature increased. The results of this study appear to confirm the suggestion that increased pyrolysis temperature reduces NH_4^+ sorption and support Zheng et al. (2010)'s findings. However, the difference between the pyrolysis

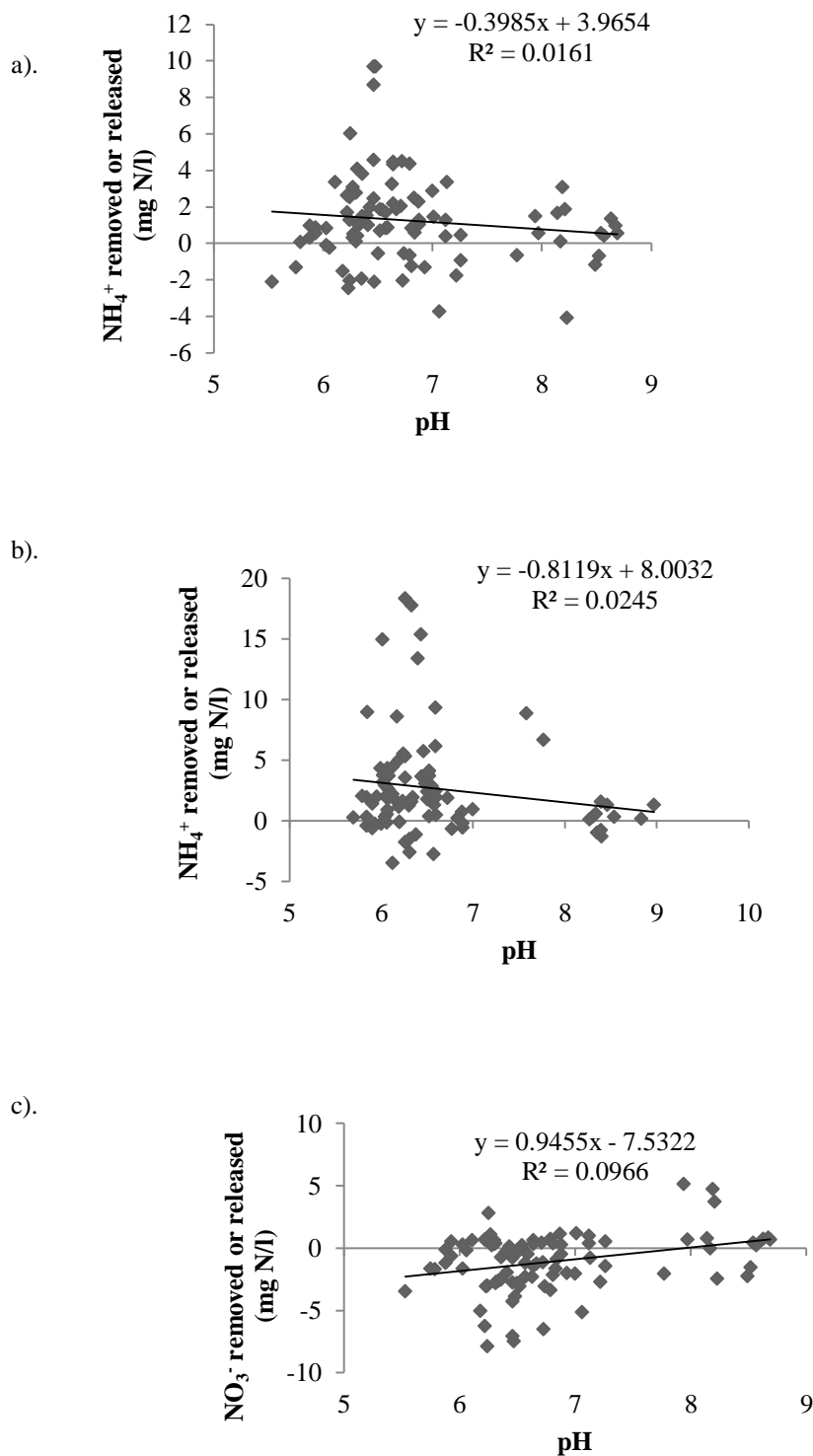
temperatures of the biochars which had highest and lowest sorption is only 50 °C so other properties are likely to also be important.

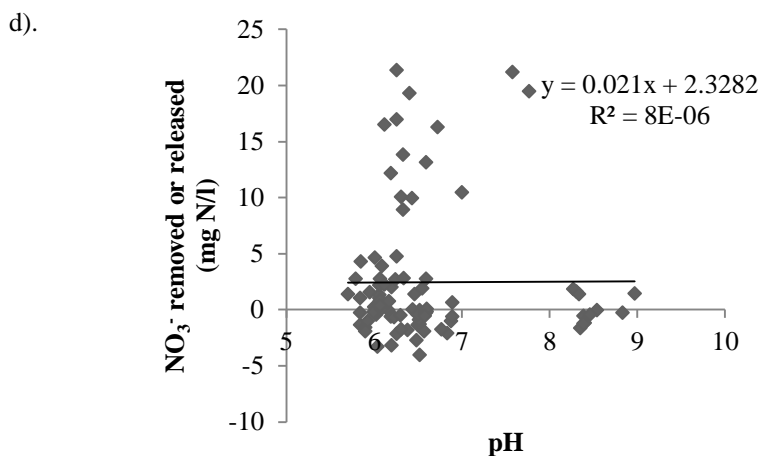
The pH of the biochars may also have been important in determining the amount of NH_4^+ sorption which occurred. Although the pH of all solutions was adjusted to between pH 5-6 after the biochar had been added, the biochar had a buffering ability and when the pH of solutions was measured again after shaking it was found that the pH of some solutions had changed. The pH of biochar is associated with its ash content, with biochars which have a higher ash content having a higher pH (Singh and Cowie, 2010). Previous work has found that an increase in reaction solution pH, for example due to displacement of surface hydroxyl groups, causes a subsequent increase in CEC (Silber et al., 2010). However, when the pH of biochars b and e, which had the highest and lowest N sorption capacities respectively are compared after shaking and reacting with NH_4NO_3 , the differences in pH are negligible suggesting that there is no pH effect on NH_4^+ sorption. Biochar c shows a consistent increase in pH after shaking to a pH of between 7-8, however biochar c demonstrated lower NH_4^+ sorption than biochars with a lower pH, in contrast to previous studies. There was no significant effect of pH on NH_4^+ sorption at either biochar particle size ($p>0.05$), indicating that pH and by association, ash content, were not influential in determining NH_4^+ sorption (Figures 2a and 2b).

Nitrate sorption was expected to be related to pyrolysis temperature of the biochar and pH. Biochar e which had a high pyrolysis temperature of 550°C (in comparison to biochars a and b) and almost neutral pH, frequently released NO_3^- from particles with <1 mm size and also had very low NO_3^- sorption at 1-4 mm particle size. This contradicts the suggestion by Kameyama et al. (2012) that the AEC of biochar may increase with increasing pyrolysis temperature due to the formation of more basic functional groups. However this suggestion was made based on comparisons of biochars produced from the same feedstock at different pyrolysis temperatures, unlike this

experiment which uses a variety of different biochars. If this was the case then it would be expected that biochar pH would increase with increasing pyrolysis temperature, however this was not evident with biochar e. Biochar c had the highest NO_3^- adsorption at 1-4 mm particle size and also high NO_3^- sorption at <1 mm particle size and although it has the same pyrolysis temperature as biochar e it has a high pH and ash content as could be seen by the increase from pH 5-6 to pH 7-8 after shaking and reacting. It is therefore likely that the high NO_3^- adsorption demonstrated by biochar c is due to its high content of base functional groups which confirms Kameyama et al's. (2012) theory. However, there was no significant relationship between pH and NO_3^- sorption at any exposure level for any biochar ($p>0.05$) (Figures 2c and 2d). It has been suggested that higher pyrolysis temperatures of biochar may increase the biochar's surface area, although this is dependent on the biochar feedstock (Ahmad et al., 2014) which could increase NO_3^- sorption. Clough et al. (2013), Mukherjee and Zimmerman (2013) and Yao et al. (2012) suggested that NO_3^- sorption is more likely to occur for biochar produced at high pyrolysis temperatures of > 600 or 650°C. The effect of pyrolysis temperature on NO_3^- sorption does not seem to be supported by the findings of our work due to the contrasting NO_3^- sorption results from biochars e and c, both of which were produced at 550°C. Instead it appears that properties (e.g. ash content, composition) of the initial feedstocks from which biochars were produced is more important.

Figure 2. a). <1mm biochar relationship between reaction solution pH after shaking and NH_4^+ sorption. b). 1-4mm biochar relationship between reaction solution pH after shaking and NH_4^+ sorption. c). <1mm biochar relationship between reaction solution pH after shaking and NO_3^- sorption d). 1-4mm biochar relationship between reaction solution pH after shaking and NO_3^- sorption





7.4.1.2 Effect of biochar particle size

It was expected that biochar particle size would affect the amount of NO₃⁻ and NH₄⁺ sorption taking place. It was hypothesised that the <1 mm diameter biochar would sorb more NO₃⁻ and NH₄⁺ than the 1-4 mm biochar as there would be a greater external surface area of biochar available for bonding of NO₃⁻ and NH₄⁺ to take place when compared to the same mass of biochar with a larger particle size. However, there was no significant difference between NO₃⁻ and NH₄⁺ sorption depending on particle size. This suggests that the internal pore structure of biochar is more important for determining NO₃⁻ and NH₄⁺ sorption than external surface area, at least over the particle size range studied in this experiment. This supports work by Hale et al. (2011) who found no significant difference between pyrene sorption to biochar at a size range of <2 mm and <75 µm and suggested that sorption capacity is mainly controlled by internal nanoporosity. However, Zheng et al. (2010) discovered that although the microporous area of biochar was important for sorption, it took longer for the sorbate to reach the microporous area of biochar which had a larger particle size, meaning that the time it

took for the biochar with a larger particle size to reach sorption equilibrium was greater. Although this could result in biochar with a larger particle size retaining less of the sorbate of interest if it is only mixed with the solution for the same amount of time as biochar of a smaller particle size, this was not evident in our experiment, demonstrating that both sizes of biochar must have reached sorption equilibrium during the time period used, perhaps indicating why no difference in NO_3^- or NH_4^+ retention between particle sizes was observed.

7.4.2 Variation between NH_4^+ and NO_3^- retention

The results indicate that all of the biochars which were tested had the ability to sorb both NH_4^+ and NO_3^- , however the magnitude of NH_4^+ sorption was generally much greater than NO_3^- sorption. The variation between the magnitude of NH_4^+ and NO_3^- sorption is likely due to the different charges and therefore mechanisms which are responsible for sorption of each ion. The high CEC of biochar has been suggested as an explanation for NH_4^+ sorption which has been observed by Ding et al. (2010), Hollister et al. (2013), Zheng et al. (2010). All of the biochars tested in this research will have had a net negative surface charge and thus a high CEC capacity, making NH_4^+ sorption by cation exchange likely to occur. Retention of NO_3^- by biochar has not been described so frequently in the literature and often has not taken place even when biochar has been exposed to N (Hollister et al., 2013), indicating that NO_3^- retention is less likely to occur.

The linear relationships obtained from the initial mass isotherms for exposure levels 1 to 5 demonstrate that larger amounts of NH_4^+ and NO_3^- were adsorbed as the initial concentration of the sorbate increased. Further analysis shows that there was also a strong positive linear relationship between the amount of NH_4^+ and NO_3^- adsorbed at each sorbate concentration by each biochar. This suggests that despite the lower magnitude of NO_3^- adsorption in comparison to NH_4^+ , the rate at which adsorption of NO_3^- and NH_4^+ increased when the concentration of added sorbate was increased is similar. The % of the initial concentration of the sorbate which was removed by the

biochar as either NH_4^+ or NO_3^- decreased as the concentration of the sorbate increased. This suggests that the affinity of biochar for NO_3^- and NH_4^+ decreased as the initial concentration of the sorbate increased, possibly due to a limited potential for sorption to take place. Hale et al. (2013) suggested that this may be due to a limited number of sites where NO_3^- and NH_4^+ could bind to the biochar. This was particularly evident when looking at NO_3^- sorption by the <1 mm biochar, which frequently retained NO_3^- at low initial concentrations of the sorbate, but showed limited retention of NO_3^- at high sorbate concentrations.

Release of the sorbate by the biochars included in this study was variable, however, it was noticed that more frequent and in general larger quantities of NO_3^- were released than NH_4^+ . The volatilization of N during pyrolysis produces biochar which has very low N concentrations such as those of 0.06 % to 0.67 % of the biochars used in this experiment. Soluble concentrations of NO_3^- in wood based biochar produced at 350°C or 800°C have been shown to be an order of magnitude smaller than those of NH_4^+ (Gundale and De Luca, 2006). Previous research has found no release of NO_3^- or lower release of NO_3^- than NH_4^+ from a variety of biochars (Hale et al., 2013; Mukherjee and Zimmerman, 2013). Therefore it is unlikely that greater amounts of NO_3^- are being released from the biochar than NH_4^+ . It is suggested that the greater and more frequently observed release of NO_3^- than NH_4^+ from the biochars is apparent due to greater sorption of NH_4^+ which would disguise any release of NH_4^+ which was occurring.

7.4.3 Implications for use of biochar in field experiments

The results of this experiment demonstrate that biochar has the ability to adsorb NH_4^+ and NO_3^- from a solution and that it may be a useful addition to agricultural soils due to its nutrient retention properties which could reduce leaching or gaseous losses of N. Soil column experiments by Ding et al. (2010) and Angst et al. (2013b) have shown that the

addition of biochar to nitrogen fertilised soils has reduced nitrogen leaching and N_2O emissions, suggesting that adsorption of N is taking place. Based on the magnitude of adsorption of NH_4^+ and NO_3^- which took place during this experiment and average soil NO_3^- and NH_4^+ concentrations it is possible to calculate the amount of adsorption that may take place in soil for a known quantity of added biochar. Addition of a nitrogen containing fertiliser to agricultural soil will increase the soil nitrogen content, however this is dependent on the amount of fertiliser added. As an example, application of 120 kg ha^{-1} NH_4NO_3 fertiliser to a Scottish agricultural soil resulted in soil mineral N peaks of around 35 mg kg^{-1} NO_3^- and 20 mg kg^{-1} NH_4^+ (as described in Chapter 5 of this thesis). The maximum NH_4^+ and NO_3^- sorption observed in this experiment were $1880 \text{ mg NH}_4^+ \text{ kg}^{-1}$ by biochar b and $1020 \text{ mg NO}_3^- \text{ kg}^{-1}$ by biochar d respectively. The maximum NH_4^+ sorption of $1880 \text{ mg NH}_4^+ \text{ kg}^{-1}$ for biochar b, is similar to that of $909 \text{ mg NH}_4^+ \text{ kg}^{-1}$ sorbed by greenwaste biochar used by Eldridge (2010) indicating that NH_4^+ sorption of this magnitude may also be possible from other biochars. If a biochar application rate of 5 tons ha^{-1} is used (as was used by Angst et al. 2014), and these adsorption rates are applied then it would theoretically be possible to remove $4.7 \text{ kg NH}_4^+ \text{ ha}^{-1}$ and $2.6 \text{ kg NO}_3^- \text{ ha}^{-1}$ from soil fertilised with $120 \text{ kg NH}_4\text{NO}_3 \text{ ha}^{-1}$ assuming that the biochar's capacity for adsorption would be the same in a field environment as it was in this experiment. However, the capacity of the biochar to retain NH_4^+ and NO_3^- would be likely to change over time, and it has been suggested that the AEC of biochars decreases as the biochar ages and oxidises in soil but that the CEC increases (Cheng et al., 2008; Singh et al., 2010).

7.5. Conclusion

This research demonstrated that biochars made from six different feedstocks had the ability to retain NH_4^+ and NO_3^- from an NH_4NO_3 solution, suggesting that the N sorption mechanism may be important in affecting N_2O emissions from biochar amended soils. Retention of NH_4^+ was generally greater than that of NO_3^- , reflecting the different mechanisms responsible for the sorption of each ion and the greater potential for sorption of NH_4^+ . Although all biochars demonstrated an affinity for NH_4^+ and NO_3^- , the capacity for retention was limited as demonstrated by decreasing amounts of NH_4^+ and NO_3^- sorption as the concentration of the sorbate increase. Release of NH_4^+ and NO_3^- was evident, with greater release of NO_3^- than NH_4^+ . However, this may reflect the greater sorption of NH_4^+ which would disguise any release of NH_4^+ occurring. There was a significant negative relationship between biochar pyrolysis temperature and NH_4^+ retention although there was only a 50 °C temperature difference between the highest and lowest pyrolysis temperatures. There was no significant effect of pyrolysis temperature on NO_3^- sorption and no significant effect of pH on NH_4^+ or NO_3^- sorption indicating that other factors such as biochar feedstock may also be important. There was no effect of biochar particle size on the magnitude of NH_4^+ or NO_3^- sorption, suggesting that the external surface area of the biochar may be less important than the internal surface area in determining sorption capacity. Calculations to estimate the potential for biochar to remove NH_4^+ and NO_3^- from N fertilised arable soils indicate that only trivial amounts of N are likely to be removed in comparison to fertiliser addition. This work reflects the need to choose biochar with specific properties which suit the purpose for which it is intended when adding it to soil and the potential to create “designer” biochars.

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Chapter 8.

Can biochar decrease greenhouse gas emissions from stored cattle slurry and slurry amended arable soil?

Can biochar decrease greenhouse gas emissions from stored cattle slurry and slurry amended arable soil?

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Abstract

This study outlines novel findings from an intensive one year field investigation of nitrous oxide (N₂O) emissions from arable soils receiving biochar which was mixed and stored alongside slurry (on a large scale) prior to application. Measurement of greenhouse gas (GHG) emissions from slurry tanks was undertaken to identify any reductions in emissions during storage. Post-application monitoring of soil GHG emissions was also carried out to see whether biochar-driven GHG mitigation processes continue in the soil environment, thereby encompassing two stages of the biochar and slurry “life cycle”. The application of a nitrification inhibitor (DCD) allowed the assessment of the potential for DCD and biochar to be used simultaneously to decrease N₂O emissions. Monitoring of slurry properties before and after storage demonstrated significant reductions in slurry NH₄⁺ and NO₃⁻ contents either with or without biochar amendment and slurry dry matter and pH were significantly increased in the biochar amended treatment. There were no significant differences in N₂O, CO₂ or CH₄ emissions from the different slurry tank treatments although the biochar amended slurry initially acted as a CO₂ sink, in contrast to the “slurry only” treatment, and also acted as an N₂O sink more frequently. There were also no significant differences between GHG emissions from “slurry only”, “slurry + biochar” and “slurry + biochar + DCD” treatments in the field experiment and no crop yield effects. The nitrification inhibitor

did not significantly decrease N₂O emissions, despite inhibiting the conversion of soil NH₄⁺ to NO₃⁻.

8.1 Introduction

Biochar has been identified as a potentially useful soil amendment for agriculture due to its stable nature, allowing it to sequester carbon (C) for timescales of up to thousands of years (Fowles, 2007). Biochar is a porous C rich solid produced when biomass is pyrolysed (Shackley and Sohi, 2010), and has a high C content which is stored in a recalcitrant chemical form. This stability means that when biochar is applied to soil, it can store C in the soil for long periods of time, thereby counteracting the release of CO₂ from anthropogenic activities (Shackley and Sohi, 2010). Other benefits which have been associated with the addition of biochar to soil include improvement of soil structure, retention of nutrients and water, enhanced crop productivity, a liming effect and of particular interest to this research, the ability to decrease greenhouse gas (GHG) emissions from soils (Johnson et al., 2007; Lehmann et al., 2006; Shackley and Sohi, 2010).

Biochar has a large surface area and usually a negative surface charge, which results in a high cation exchange capacity (CEC), perhaps accounting for the observed ability of biochar to retain NH₄⁺ from solution (Thesis chapter 7; Yao et al., 2012). Biochar has also been demonstrated to retain NO₃⁻, although to a lesser extent than NH₄⁺ (Yao et al., 2012) with suggested mechanisms including anion exchange (Kameyama, 2012), retention in solution in biochar pores (Prendergast-Miller, 2011), or bridge bonding (Mukherjee, 2011). The retention of both NH₄⁺ and NO₃⁻ by biochar has been further explored in relation to the potential for biochar to decrease NH₄⁺ and NO₃⁻ leaching from soils, thereby conserving N within the soil which provides agronomic benefits in the form of potential greater crop growth. Soil column experiments have demonstrated decreased leaching of NH₄⁺ and NO₃⁻ from soils amended with a range of biochars, supporting the theory that biochar is able to retain NH₄⁺ and NO₃⁻ (Angst et al., 2013a; Ding et al., 2010; Kameyama et al., 2012; Yao et al., 2012).

The ability of biochar to retain N and the observed reduction in leaching of NH_4^+ and NO_3^- from biochar amended soils has led to research into the potential for biochar to act as an N_2O mitigation tool for N fertilised soils. Nitrous oxide is a powerful GHG which also depletes the ozone layer. Decreases in N_2O emissions from biochar amended soils have been observed, although the majority of this evidence stems from laboratory work, with little fieldwork yet having taken place to confirm laboratory findings. Various mechanisms have been proposed to account for the decreases in N_2O emissions observed from biochar amended soils. The retention of N by biochar, is one such mechanism and it is proposed that by retaining NH_4^+ and NO_3^- , biochar decreases the availability of these nutrients to the nitrifying and denitrifying bacteria, thereby decreasing N_2O production. Angst et al. (2013a) and Singh et al. (2010) observed significant decreases in N_2O emissions from biochar amended soils. The combination of these decreases in N_2O emissions with decreased N leaching, led to suggestions that the decreased N_2O emissions were due to retention of N by the biochar. An alternative mechanism which may decrease N_2O production in biochar amended soils, is the alteration of soil physical properties such as aeration by the biochar which decreases WFPS and the potential for denitrification to take place. Rogovska et al. (2011) and Van Zwieten et al. (2010) suggested that this mechanism was responsible for decreased N_2O emissions from their biochar amended soils. However, this theory has been refuted by Case et al. (2012) who demonstrated that increased aeration had only a minimal effect on N_2O emissions and was not the only mechanism responsible. The liming effect of biochar due to its high ash content has also been suggested to decrease N_2O emissions by promoting the reduction of N_2O to N_2 during the denitrification pathway (Cayuela et al., 2013; Clough et al., 2010; Van Zwieten et al., 2010). Yanai et al. (2007) observed no effect on N_2O emissions from soils amended with only ash and therefore rejected the pH mechanism as a means by which N_2O emissions are decreased. However, Cayuela et al. (2013) demonstrated that in biochar amended soils, greater reduction of N_2O to N_2 took place (i.e. the final stage of denitrification). Although this is more likely to occur under high pH conditions, Cayuela et al. (2013) suggested that the biochar was acting as an “electron shuttle” or electrical conduit, assisting the movement of electrons to N_2O

reducing bacteria, thereby enhancing the reduction of N_2O . Although biochar has often demonstrated the ability to decrease N_2O emissions from soils, this effect is not consistent across all types of biochar due to variations in physical and chemical biochar properties which are associated with differences resulting from source feedstock and pyrolysis conditions (Singh et al., 2010). Other biochar properties including biochar age, particle size and pyrolysis temperature have demonstrated a control on nutrient retention and N_2O emissions (Angst and Sohi, 2012; Hollister et al., 2013; Singh et al., 2010). This indicates that if biochar is to be used to successfully decrease N_2O emissions from soils, we must first understand the specific properties of biochar which are affecting N_2O emissions and then use this knowledge to select biochars which have the greatest potential to decrease N_2O emissions in the field environment. Nitrification inhibitors are another potential N_2O mitigation option which act to decrease N_2O production by nitrification through inhibition of the oxidation of NH_3 to NO_3^- (Di and Cameron, 2002). Little research has been carried out to assess the effect on N_2O emissions of applying both a nitrification inhibitor and biochar to N fertilised soils, although Hagemann et al. (2014) observed decreases in N_2O emissions from N fertilised soils amended with beech wood biochar both with and without the presence of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP). It is hypothesised that due to the inhibition of nitrification by a nitrification inhibitor, plus the potential inhibition of nitrification and/or denitrification by biochar, then applying both a nitrification inhibitor and biochar to soil should result in a greater decrease in N_2O emissions than if only one amendment was applied.

Despite the potential for biochar to decrease N_2O emissions and N leaching from soil, biochar application to agricultural land is not widely practiced. This is due to a lack of solid evidence from field research resulting from constraints imposed by mechanical and human health considerations. Additionally, most field trials which have taken place have been small scale where it has been appropriate to apply biochar by hand. The application of biochar to the large scale field environment needs to take into account

issues such as the preparation and transportation of the biochar, in addition to the application method and incorporation into the soil. (Shackley and Sohi, 2010). One of the key issues associated with biochar application to the field relates to the fine particulate nature of biochar which poses a risk in terms of loss of biochar during and after application due to transport by wind and water and also health issues related to potentially carcinogenic dust from the biochar. Suggested methods to overcome these issues include pelleting the biochar, mixing of biochar and liquid fertiliser, addition of biochar to animal feed, injection of biochar beneath the soil surface or addition of water to the biochar to decrease dust availability (Shackley and Sohi, 2010; Van Zwiiten et al., 2010). The economics of spreading biochar must also be taken into account, which makes it desirable to co-apply biochar and fertiliser to minimise fuel usage but also to decrease issues such as soil compaction. Co-application of biochar and slurry in organic farming systems has been suggested as a practical means by which biochar may be applied to soil (Shackley and Sohi, 2010) but experimental evidence to support this practice is lacking.

Livestock production is an important agricultural activity and covers 30 % of the total land area of the Earth, in addition to producing 18 % of CO₂ eq GHG emissions (FAO, 2006). Livestock production inherently involves the production of livestock waste, some of which is subsequently used as fertiliser due to its high N content. Cattle slurry is one such livestock waste and is commonly stored for long periods of time before being applied to soil, during which it emits the GHGs CO₂, CH₄ and N₂O (Angst et al., 2013b, Sommer et al., 2000). The addition of a natural crust to stored slurry has been observed to reduce GHG emissions (Sommer et al., 2000) and Angst et al. (2013b) observed significant reductions in N₂O, CO₂ and CH₄ emissions when biochar was mixed with stored slurry to form an even thicker crust. However, this work was on a small scale with containers holding only 1.5 L of slurry and slurry was not applied to soil following the experiment to see if the GHG mitigating effect was continued in the soil. The work

by Angst et al. (2013b) is the only known research into the use of biochar to decrease GHG emissions from stored slurry.

To the best of our knowledge, application of biochar-amended slurry to arable soils has not previously been investigated in this level of detail in the field. The specific aims of this experiment were to assess whether biochar can decrease N_2O , CO_2 and CH_4 emissions from stored slurry and whether any GHG mitigation from the slurry tanks continues following application of the slurry and biochar mixture to a field experiment. The potential for combined use of a nitrification inhibitor (DCD) and biochar-amended slurry to decrease N_2O emissions from the field experiment, alongside any potential agronomic improvements were investigated.

8.2 Materials and Methods

8.2.1. Biochar and slurry storage

The biochar used in this study was produced at the UK Biochar Research Centre from oil seed rape straw pellets, a commonly available local feedstock, at a pyrolysis temperature of 550 °C. The oilseed rape straw biochar was selected after testing of the NH_4^+ and NO_3^- retention abilities of 6 biochars during a batch sorption experiment (described in Chapter 7). The oil seed rape straw biochar showed the greatest capacity to retain both NH_4^+ and NO_3^- and was therefore chosen for use in this experiment as it was predicted to have the greatest potential to decrease N_2O emissions. Biochar properties are shown in Table 1. Locally sourced cattle slurry (300 L per tank) was put into 12 tanks, each with 1000 L capacity, with six tanks designated as “slurry only” and six “slurry + biochar”. Biochar was added to the slurry at a mass ratio of 1:2 slurry dry matter to biochar, resulting in a biochar application rate of 19 kg biochar/tank. Slurry pH, redox potential, dry matter, total N, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and total C contents were measured at the beginning and end of slurry storage. The slurry tanks were stored on the ground in a barn, so were subject to variations in air temperature but were sheltered from precipitation. During storage, tank lids were left partly open, except for during gas sampling, to allow exchange of gases from the slurry tank with the atmosphere, but to minimise moisture losses.

Table 1. *Oil seed rape straw biochar properties*

Biochar properties	
Pyrolysis temperature °C	550
Total C content %	67.84
Labile C (% of total C)	0.18
Total N content %	0.30
pH	8.44
Moisture %	4.12
Ash content %	18.30

Emissions of N_2O , CO_2 and CH_4 were measured 15 times over a 50 day period using an adapted static closed chamber methodology (Chadwick et al., 2014). On each sampling occasion, the slurry tank lids were closed for 40 minutes and a gas sample taken at zero minutes and again at 40 minutes after lid closure to measure gas accumulation within the tank over the 40 minute period. Sampling ports were installed in each slurry tank lid to extract gas samples, using a syringe, into pre-evacuated 20-22ml glass vials. The headspace height of each slurry tank and the air temperature in the barn in which the slurry tanks were stored was measured on each sampling occasion for use in gas flux calculations. N_2O , CH_4 and CO_2 concentrations were measured using an Agilent 7890A Gas Chromatograph (GC) fitted with an electron capture detector (ECD), a thermal conductivity detector (TCD), a flame ionisation detector (FID) and a CTC Analytics COMBI PAL autosampler (CTC Analytics, Hampshire, UK).

8.2.2. Field experiment

The contents of the slurry tanks were applied to field plots at Boghall farm in Eastern Scotland in April 2013 after 50 days of storage. Site characteristics are described in Table 2. The field plots measured 6 x 12 m and were replicated in triplicate in a randomised block design, including a control. Treatments were applied at a rate of 41,000 L ha⁻¹ (50 kg N ha⁻¹). The following treatments were applied, to assess the impact of biochar application and nitrification inhibitors: slurry (surface broadcast application), slurry + biochar (surface broadcast), slurry + biochar + nitrification inhibitor DCD (surface broadcast). These treatments were abbreviated to SSB, SB and SBDCD, respectively, plus the control (CON). The nitrification inhibitor was sprayed onto the plots at a rate of 10 kg ha⁻¹, one hour after slurry application. Pesticides and herbicides were applied throughout the field experiment in accordance with standard recommendations.

Emissions of N_2O , CO_2 and CH_4 were measured frequently for a year following application using the static closed chamber technique (Chadwick et al., 2014). Sampling took place between 10.00- 12.00 on all occasions to limit any bias from temporal variation, and the intensity of sampling frequency decreased over time, to take into account the higher emissions associated with the period immediately following fertiliser application (Dobbie et al., 1999). In total, GHG emissions were measured 30 times over a 12 month period. Five opaque plastic chambers measuring 0.16 m^2 were inserted 5 cm into the soil on each plot, giving a total of 15 chambers per treatment. The chambers remained in place throughout the experiment except for removal during agricultural operations. Additional chambers were stacked on top of the original chambers during crop growth to avoid damaging the growing crops. During sampling, the chambers were closed for 40 minutes and samples were taken using a syringe through a sampling port in the chamber lid. Ten ambient gas samples were collected on each measurement occasion and the linearity of gas accumulation in 3 randomly selected chambers was also checked (Chadwick et al., 2014). N_2O , CO_2 and CH_4 concentrations were analysed using the method described in section 8.2.1.

Table 2. *Boghall site characteristics*

Site characteristic	Description
Elevation	195 m
30 year mean precipitation	849 mm
40 year mean air temperature (January)	4°C
40 year mean air temperature (July)	13°C
Total precipitation (April 2013-April 2014)	1368 mm
Mean air temperature (April 2013- April 2014)	8.19 °C
Soil texture	Sandy loam
Soil series	Darvel
Soil pH	6
Soil organic matter	6%
Average soil bulk density	1.08 g cm ⁻³
Crop type	Winter wheat (Grafton)
Sowing date	25 th October 2012
Sowing rate	400 m ⁻²
Harvest date	5 th September 2013
Crop 2010	Spring barley
Crop 2009	Spring barley
Crop 2008	Spring barley

On each sampling occasion, five soil samples (0-10 cm depth) were collected from each block for soil gravimetric water content determination. Soil bulk density was measured regularly throughout the experiment following the collection of intact soil samples using metal rings. Soil bulk density measurements and soil gravimetric water content were then used to calculate soil water filled pore space (WFPS). At approximately monthly intervals, 5 soil samples per plot were collected and combined (giving one sample per plot) for soil mineral N (NH₄⁺ and NO₃⁻) analysis. Soils sieved to <4 mm were extracted using 2 M KCl and soil NH₄⁺ and NO₃⁻ concentrations in extracts were determined using a Skalar San⁺⁺ continuous flow autoanalyser (Skalar, York, UK).

Daily weather conditions at the field site were measured using a weather station which remained in situ, and on each sampling occasion soil temperature at 10 cm depth and air temperatures were also measured (RS Components, Northamptonshire, UK). Following harvest of the plots (15 m² from each plot) using a small plot harvester, and collection of 100 tillers per plot by hand, the crop yield, the N content and % dry matter of the grain, straw and chaff were recorded.

8.2.3 Data analysis

Daily fluxes of N_2O , CO_2 and CH_4 from the slurry tanks and field experiment were calculated using linear regression, which assumes that the increase in gas accumulation within the slurry tank or chamber is linear over a 40 minute closure time (Chadwick et al., 2014; Saggar et al., 2008). Although the increase in gas accumulation from the slurry tanks was assumed to be linear, this theory was not tested. However, previous similar work by Angst et al. (2013b) took samples to test for linearity and also used linear regression to calculate gas GHG fluxes. The trapezoidal rule was then used to interpolate fluxes between sampling days to provide cumulative N_2O , CO_2 and CH_4 fluxes from each tank or chamber. Treatment cumulative fluxes were then calculated using the mean of the 6 tanks per treatment for the tank experiment, or from the mean of 3 plots in the field, following the calculation of the mean from the 5 chambers on each plot. One way analysis of variance (ANOVA) was used to assess treatment effects on cumulative emissions from the slurry tanks, and two way ANOVA was used to assess treatment effects on cumulative emissions from the field experiment, also taking into account the effects of blocks. CO_2 equivalent emissions for CH_4 and N_2O were calculated using global warming potentials of 25 for CH_4 and 296 for N_2O (IPCC, 2006)).

8.3. Results and discussion

8.3.1 Slurry tank experiment

8.3.1.1 Slurry properties

Significant changes in several aspects of the slurry's properties were observed for both treatments over the experimental storage period (Table 3). The slurry only treatment saw significant decreases in $\text{NH}_4^+\text{-N}$ ($p < 0.05$), $\text{NO}_3^-\text{-N}$ and total C ($p < 0.01$), and the slurry + biochar treatment showed significant decreases in $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ ($p < 0.01$) and a significant increase in dry matter (DM) content ($p < 0.01$). The decrease over time in $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ content observed in both treatments was likely due to emissions of N_2O from the slurry depleting the pools of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$, but possibly also retention of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ by the biochar. Based on the results of the work described in Chapter 7, it was calculated that the biochar added to each slurry tank had the ability to remove 8 % and 40 % of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ respectively. It is not known how much $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ was retained by the biochar in the slurry tanks but concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ decreased by 29 % and 80 %, respectively. Additionally, although not measured it is likely that NH_3 emissions also depleted the slurry N content as previous research demonstrated large emissions of NH_3 from stored slurry (Amon et al., 2006). CO_2 and CH_4 emissions from the slurry were responsible for the decrease in C content of the slurry only treatment. It was assumed that degradation of added labile C from the biochar, which was only 0.18 % of the total biochar C (Table 1) was minimal and did not compensate for any C lost through emissions. The significant increase in slurry DM content in the slurry + biochar treatment post-biochar addition reflects the high biochar DM content of 96 %, perhaps alongside the ability of the biochar to physically absorb liquid through its porous structure. The observation of the biochar floating at the surface of the slurry and forming a crust may also explain the increase in DM as the crust may have decreased the amount of water vapour escaping from the slurry (Angst et al., 2013b; Lehmann et al., 2009).

Slurry properties were also assessed for any variation between treatments, at the beginning and end of the experiment, respectively. At the beginning of the experiment there were no significant differences, however, at the end of the experiment there was a significantly greater amount of DM in the slurry + biochar treatment than the slurry only treatment (Table 3) (3.08 % compared to 1.62 %) and significantly higher slurry pH in the slurry + biochar treatment (7.52 compared to 6.86) ($p < 0.01$). There was no significant difference in redox potentials between treatments at the end of the experiment ($p < 0.01$). Total N content was also significantly higher in the slurry + biochar treatment in comparison to the slurry only treatment (0.12 % compared to 0.11 %) in addition to greater total C content in the slurry + biochar treatment (36.03 as % DM compared to 32.88 as % DM) ($p < 0.05$). The effect of biochar on slurry DM and C content as mentioned previously will also have caused these observed differences between treatments. The significant difference in slurry pH can be explained by the high ash content (18.2 %) and pH (8.44) of the oil seed rape straw biochar that was added to the slurry (Table 1). The significantly greater total N content of the slurry + biochar treatment is suggested to be due to retention of N, either in the form of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ by the biochar, as sorption of N by biochar has previously been reported by Ding et al. (2010), Kameyama et al. (2012), Lehmann et al. (2002) and Yao et al. (2012). The oil seed rape straw biochar used in this experiment has previously demonstrated the capacity to retain considerable quantities of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ through a laboratory batch sorption experiment (described in Chapter 7), and this is likely to have occurred when the biochar was mixed with slurry. Previous work by Angst et al (2013b) has also demonstrated possible retention of N by biochar mixed into slurry, as significantly greater $\text{NO}_3^-\text{-N}$ contents were found in comparison to a control.

Table 3. a). Mean slurry properties at start of experiment (before addition of biochar) b). Mean slurry properties at end of experiment (prior to application to field)

a). Start of experiment

	Dry matter (%)	pH	Total N (mg kg ⁻¹)	NH ₄ ⁺ -N (mg kg ⁻¹)	NO ₃ ⁻ -N (mg kg ⁻¹)	Total C (mg kg ⁻¹)
“Slurry only” tanks: Start of experiment	1.5 ^a	7.31 ^a	1300 ^a	640 ^a	400 ^a	5430 ^a
Slurry + biochar tanks: Start of experiment	1.5 ^a	7.31 ^a	1300 ^a	780 ^a	500 ^a	5610 ^a

b). End of experiment

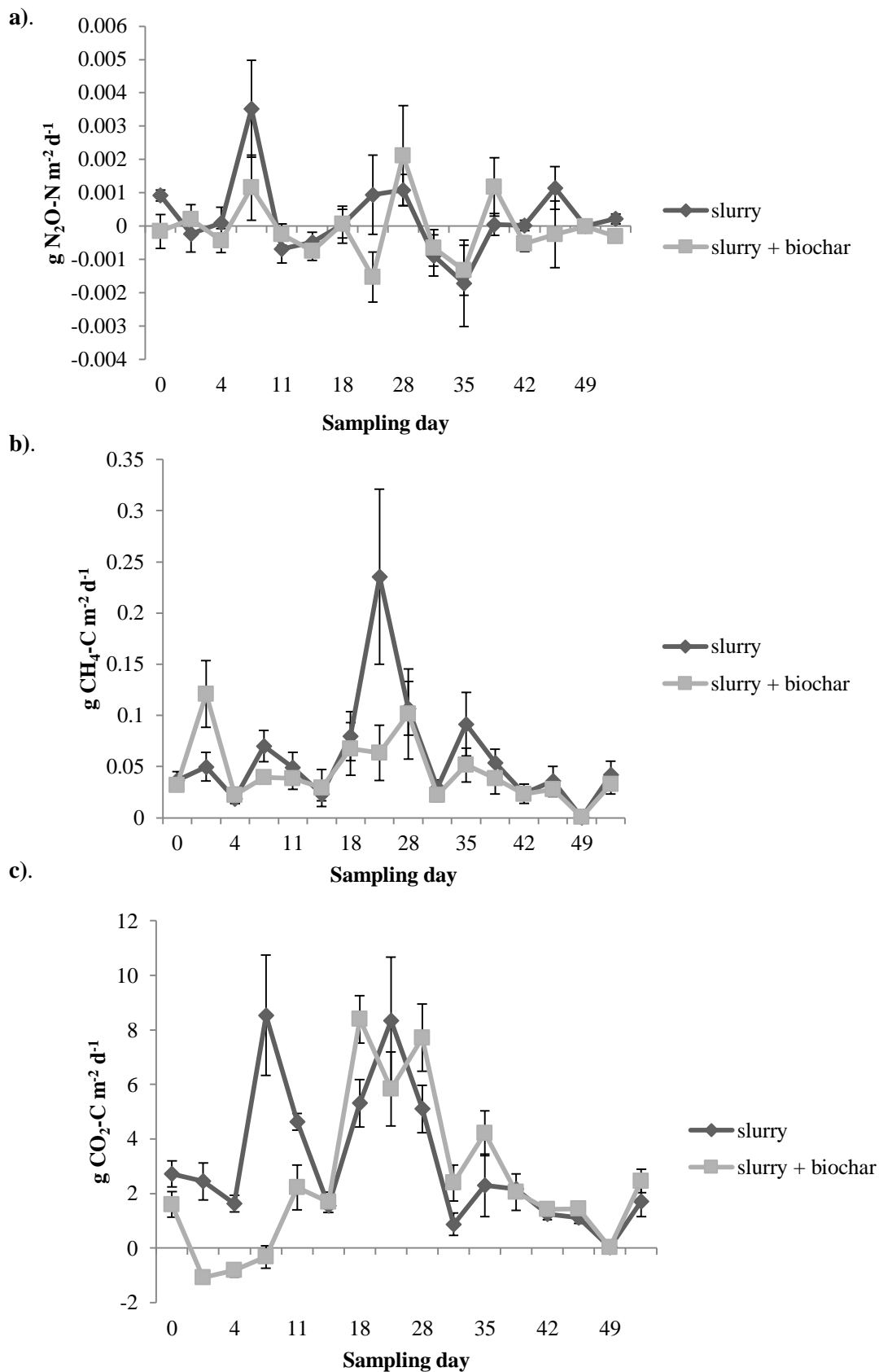
	Dry matter (%)	pH	Total N (mg kg ⁻¹)	NH ₄ ⁺ -N (mg kg ⁻¹)	NO ₃ ⁻ -N (mg kg ⁻¹)	Total C (mg kg ⁻¹)	Redox potential Eh (mV)
“Slurry only” tanks: End of experiment	1.6 ^a	6.89 ^a	1100 ^a	530 ^a	<100 ^a	5264 ^a	-257.33 ^a
Slurry + biochar tanks: End of experiment	3.1 ^b	7.52 ^b	1200 ^b	550 ^a	<100 ^a	11160 ^b	-252.00 ^a

Different letters after values indicate a significant difference between treatments at the same time period

8.3.1.2 Slurry tank GHG fluxes

Greenhouse gas fluxes from both treatments varied throughout the measurement period (Figure 1). The variation in the rates of GHG production are due to the dependence of these processes on the substrate (e.g. C and N) concentrations and controlling variables such as slurry moisture content and temperature (Rodhe et al., 2009). Nitrous oxide emissions were low throughout ranging from a maximum of $0.0035 \text{ g m}^{-2} \text{ d}^{-1}$ from the slurry only treatment on day 7 to a minimum of $-0.0017 \text{ g m}^{-2} \text{ d}^{-1}$ from the slurry only treatment on day 35. Negative N_2O emissions i.e. the slurry was acting as an N_2O sink, occurred more frequently for the slurry + biochar treatment for which negative N_2O emissions were recorded 11 times, compared to the slurry only treatment where negative N_2O emissions were recorded 5 times. Methane emissions were also low ranging from a minimum of $0.00049 \text{ g m}^{-2} \text{ d}^{-1}$ for the slurry only treatment on day 49, to a maximum of $0.24 \text{ g m}^{-2} \text{ d}^{-1}$ for the slurry only treatment on day 25. Both treatments acted as a source of CH_4 throughout the experiment. Carbon dioxide ranged from a minimum of $-1.08 \text{ g m}^{-2} \text{ d}^{-1}$ for the slurry + biochar treatment on day 1, to a maximum of $8.53 \text{ g m}^{-2} \text{ d}^{-1}$ from the slurry only treatment on day 7. The slurry only treatment always acted as a CO_2 source, however the slurry + biochar treatment acted as a CO_2 sink from day 1-7, after which it was a source of CO_2 . After day 35, CO_2 emissions from both treatments appeared to be tailing off.

Figure 1. Slurry tank daily GHG fluxes during the experimental period a). N_2O b). CH_4 c) CO_2



There were no significant differences in mean cumulative emissions of N_2O , CH_4 and CO_2 between the treatments, although there was a large amount of variation in emissions between tanks (Table 4). Greater CH_4 emissions were observed for the “slurry + biochar” tanks but they were not significantly different from the control tank emissions. This finding was in contrast to Angst et al. (2013b) who found significantly higher CH_4 emissions from their slurry + biochar treatment than from the control during their laboratory experiment. However, Angst et al. (2013b) measured emissions for double the time period of this experiment (~ 100 days) and obtained CH_4 emissions which were an order of magnitude greater, which may account for more noticeable differences between treatments.

Although there were no significant differences in cumulative emissions of CO_2 between treatments, the biochar + slurry treatment initially produced very low CO_2 emissions or acted as a CO_2 sink. A possible mechanism by which the addition of biochar to slurry could decrease CO_2 emissions is by the formation of a biochar crust on the surface of the slurry (Angst et al., 2013b). In this experiment the biochar was observed to float at the surface of the slurry, however, if a crust was present it would also decrease CH_4 emissions and this did not occur, and a crust would also not explain why the slurry appeared to be taking up CO_2 . On the first day of measurements following biochar addition to the slurry, there was a considerable peak in CH_4 emissions from the slurry + biochar treatment in comparison to the slurry only treatment. At this time the slurry + biochar treatment was also acting as a sink for CO_2 . This suggests that methanogenesis was taking place, as methanogens use CO_2 during the production of CH_4 (Cloy et al., 2012). The availability of labile carbon from the biochar (approximately 23 g per tank) may have enhanced rates of methanogenesis in the slurry + biochar treatment, causing the CO_2 sink effect observed in the slurry + biochar treatment.

Table 4. Table of cumulative N_2O , CH_4 , CO_2 and CO_2 eq emissions from the tank and field experiments

Treatment	N_2O g m⁻²	CO_2 equivalent g m⁻²	CH_4 g m⁻²	CO_2 equivalent g m⁻²	CO_2 g m⁻²
A Slurry only	0.015	4.30	3.49	87.19	185.15
A Slurry + biochar	-0.0045	-1.33	6.22	155.44	156.88
B SBD CD	0.0061	1.81	-0.59	-14.65	442.27
B SSB	-0.0084	-2.47	-0.16	-3.96	422.30
B SB	-0.0035	-1.020	-0.057	-1.43	350.01
B CON	0.04045	11.97	-0.48	-11.88	636.57
C Slurry only	0.0066	1.83	3.33	83.23	607.45
C Slurry + biochar	-0.008	-2.35	6.163	154.01	506.89

A= tank experiment

B= field experiment

C= overall comparison

CO_2 equivalent calculated using GWPs of 25 for CH_4 and 296 for N_2O (IPCC)

No significant differences between any treatments ($p < 0.05$)

The lack of significant differences between the treatments in comparison to previous work using the same ratio of slurry to biochar (Angst et al., 2013b), perhaps reflects the differences in scale of the experiments and the variations between different types of biochar. This experiment used 200 times the volume of slurry used by Angst et al. (2013b) in each slurry container, resulting in a greater area of slurry being in contact with the air. The greater slurry surface area meant that a larger surface area of biochar crust formed. Petersen et al. (2005) proposed that CH₄ oxidation may take place in a slurry surface crust and the large crust present could therefore be mitigating any CH₄ enhancement effect caused by the biochar as seen by Angst et al. (2013b), therefore creating negligible differences between treatments. Oxidation of CH₄ produces CO₂ (Sommer et al., 2007) and again, the large surface area of slurry crust present could be counteracting any decrease in CO₂ caused by the slurry as observed by Angst et al. (2013b).

The mean cumulative emissions of N₂O from the slurry and biochar treatment was close to 0, supporting the theory that the biochar may have retained N and thereby decreased its availability for transformation into N₂O. However, in contrast to Angst et al. (2013b), there was no significant decrease in N₂O emissions associated with the biochar treatment. It is therefore suggested that although the biochar retained N, the N was still available for transformation into N₂O, although the biochar possibly decreased N availability as the greater total N content of the biochar + slurry treatment was not associated with increased N₂O emissions. The biochar was observed to float at the surface of the slurry, forming a crust. Previous research has demonstrated that both oxic and anoxic conditions can be present in such a crust, allowing the production of N₂O by both nitrification in the oxic areas and denitrification in the anoxic areas (Huther et al., 1997). A proposed mechanism by which the biochar + slurry mixture may be acting as a sink for N₂O is through N₂O being consumed during the denitrification pathway. The N₂O reductase enzyme which reduces N₂O to N₂ during denitrification is inhibited under low pH conditions (Chapuis and Lardy, 2007). The significantly greater pH in the

biochar + slurry treatment (Table 3) may therefore be stimulating greater reduction of N_2O to take place. The “electron shuttle” mechanism proposed by Cayuela et al. (2013) by which the biochar assists in moving electrons to N_2O reducing bacteria is also suggested to occur under high pH conditions. Angst et al. (2013b) also proposed that the increase in slurry pH caused by the addition of biochar, was perhaps responsible for decreased N_2O emissions. Research into N_2O consumption in soils has suggested that if gas diffusivity across the soil-air interface is decreased then N_2O consumption may take place (Arah et al., 1991). If the same is true for slurries then then formation of a biochar layer at the surface of the slurry may be decreasing gas diffusivity leading to a subsequent increase in N_2O consumption. The GHG data presented relies on the assumption that the increase in gas accumulation over the 40 minute tank closure period was linear. However, as this was not tested, caution must be used when interpreting this data.

8.3.2 Field experiment

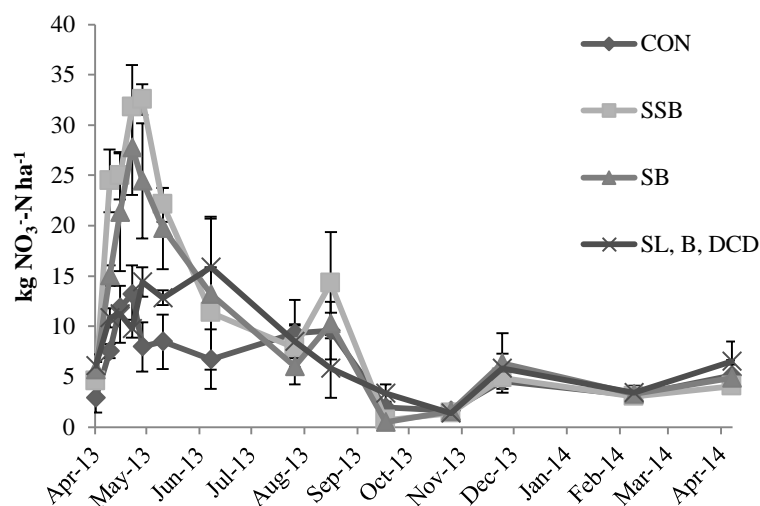
8.3.2.1 Soil mineral N

Soil NO_3^- -N contents increased rapidly following fertilisation, with a peak in soil NO_3^- -N contents occurring for all treatments between 25th April 2013- 10th May 2013 with a maximum value of 33 kg N ha⁻¹ from the slurry only treatment (Figure 2). Soil NO_3^- -N contents were generally lower in the SB and SBDCD treatments in comparison to the SSB treatment. The SBDCD treatment had lower soil NO_3^- -N contents than the SB treatment. Soil NO_3^- -N contents returned to background levels (<5 mg N kg⁻¹ soil, or approximately 9 kg N ha⁻¹) approximately 5 months after fertilisation. Soil NH_4^+ -N contents increased following fertiliser application, although not as rapidly as the increase in soil NO_3^- -N (Figure 2). Peaks in soil NH_4^+ -N contents for the SSB and SB treatment were observed within the first week of the experiment with values of 4 kg N ha⁻¹ and 2 kg N ha⁻¹, respectively. Soil NH_4^+ -N contents for all treatments except the SBDCD treatment remained below 6 kg N ha⁻¹ for the duration of the experiment, with the

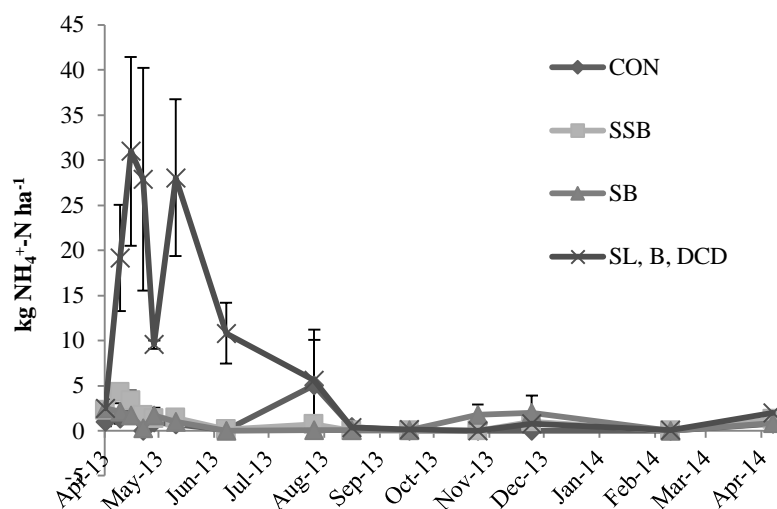
SBD CD treatment returning to below this level on 19th August, after which soil $\text{NH}_4^+\text{-N}$ contents for all treatments remained below 2 kg N ha⁻¹. The SBD CD treatment peaked on 18th April with a value of 31 kg N ha⁻¹ and the CON treatment $\text{NH}_4^+\text{-N}$ content peaked on 29th July with a value of 5 kg N ha⁻¹. The SBD CD treatment had consistently higher soil $\text{NH}_4^+\text{-N}$ contents than all the other treatments as has also been demonstrated in nitrification inhibitor experiments by Di and Cameron (2002, 2003). The greater $\text{NH}_4^+\text{-N}$ and lower $\text{NO}_3^-\text{-N}$ contents in the SBD CD treatment in comparison to other treatments demonstrates the effectiveness of the nitrification inhibitor in decreasing nitrification rates.

Figure 2. Soil mineral N contents during the experimental period. a) NO_3^- b) NH_4^+

a).



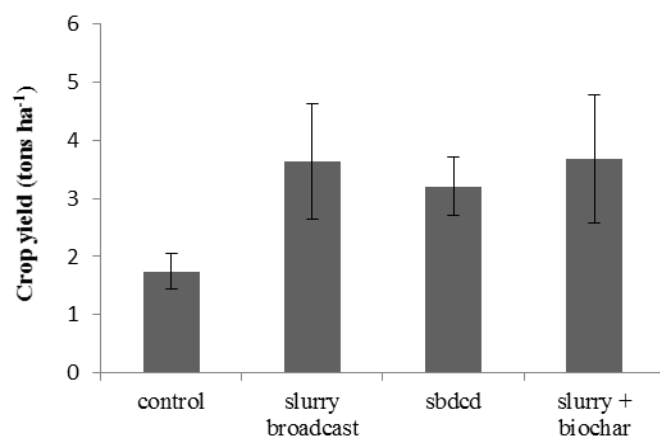
b).



8.3.2.2 Crop yield

Mean grain yields ranged from a minimum of 1.75 t ha⁻¹ from the CON treatment to a maximum of 3.68 t ha⁻¹ from the SB treatment (Figure 3). Crop yields were atypical for the area due to issues associated with late sowing as a result of poor weather and soil conditions, and destruction of the crop by birds. There was no significant difference in crop yields between any of the treatments ($p < 0.05$). It would be expected that the fertilised treatments would increase crop yield relative to the CON treatment, however, a large amount of N is lost from organically fertilised soil in the form of NH₃ and also N₂O (Rodhe et al., 2006), therefore reducing the amount of N available for crop growth. Although NH₃ emissions were not measured in this experiment, a similar experiment using the same slurry recorded NH₃ emissions which accounted for about 20 % of applied N (described in Chapter 6). If this value is combined with the amount of N lost via N₂O emissions, approximately 21 % of N was lost from the slurry fertilised treatments in this experiment. This combined with large variability in yield from treatment plots may account for the lack of difference in yield between the CON and other treatments.

Figure 3. *Crop yield for 2013 harvest.*



The use of a nitrification inhibitor has often been reported to increase crop yield due to maintenance of higher levels of N in the soil (Di and Cameron, 2002; Liu et al., 2013). However, this effect was not observed in this experiment despite the nitrification inhibitor amended treatment enhancing NH_4^+ -N levels in the soil. This reflects the preferential uptake of NO_3^- rather than NH_4^+ by plants (Hofman and van Cleemput, 2004) in addition the high variability in crop yields between plots and the general poor growth rate of plants.

8.3.2.3 GHG fluxes

Nitrous oxide emissions were close to zero throughout the field experiment in all treatments (Figure 4). There were no significant differences between any treatments. It was hypothesised that the biochar amended treatments would decrease N_2O emissions as has been observed in other studies (Felber et al., 2014; Liu et al., 2012; Taghizadeh-Toosi et al., 2011), due to retention of soil and slurry N by the biochar therefore decreasing the availability of N for nitrifiers and denitrifiers. The addition of a nitrification inhibitor to slurry + biochar (SBDCD treatment) was expected to further enhance the decrease in N_2O emissions due to inhibition of the nitrification pathway of N_2O production, as has been effectively demonstrated previously by Merino et al. (2002) and Vallejo et al. (2005) who amended slurry applications with DCD. The lack of effectiveness of the nitrification inhibitor is in agreement with Merino et al. (2001) and Mkhabela (2006) who found no significant differences in N_2O emissions when slurry applications to soil were amended with the nitrification inhibitor DCD. A potential cause of the ineffectiveness of the nitrification inhibitor in this study is the organic matter content of the soil and the organic nature of the fertiliser. The presence of large amounts of organic matter has been suggested to decrease the effectiveness of DCD through increasing microbial degradation of the DCD and sorption of DCD to the organic matter (Slangen and Keerhoff, 1984). It was also proposed by Prasad and Power (1995) that nitrification inhibitors are ineffective when used on soil with organic matter contents >5

%. The organic matter content of the soil used in this experiment was 6.6 %, which may have limited the effectiveness of the nitrification inhibitor in this case.

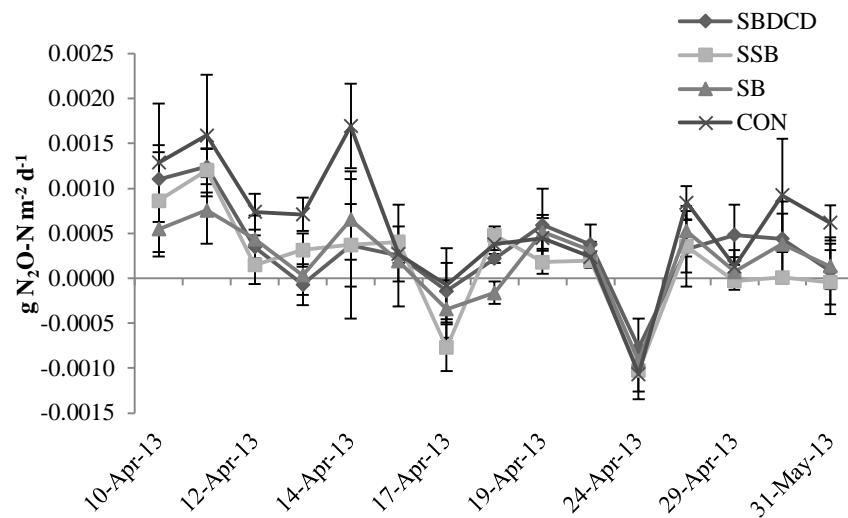
However, it is most likely that the lack of difference in N₂O emissions between the nitrification inhibitor amended treatment and the non amended treatments is due to the very small N₂O emissions associated with all treatments. N₂O emissions were much lower than have previously been recorded in comparable experiments (around 3 times and 18 times smaller, respectively, than those reported by Rodhe et al. (2006) and Perala et al. (2006)). The low N₂O emissions mean that although the nitrification inhibitor may be decreasing nitrification rates (as demonstrated by the enhanced soil NH₄⁺-N concentrations and decreased NO₃⁻-N concentrations in Figure 4), there was so little N₂O being produced by either nitrification or denitrification that any effect of the nitrification inhibitor on N₂O emissions would be negligible. The low N₂O emissions are likely to be associated with the weather conditions during the experiment. In general, the experimental period was very dry, with little rainfall occurring and low soil moisture. Soil WFPS ranged from 24-52 %, with a mean value of 40 %. Maximum N₂O emissions are considered to occur between 50-70 % WFPS (Davidson, 1991) and below 65-75 % nitrification is the dominant N₂O producing process (Scheer, 2011) with optimum conditions for nitrification occurring between 40-65 % (Merino et al., 2001). This indicates that the low soil moisture recorded in this experiment may have limited N₂O production. Some N₂O emissions also occurred after the return of soil mineral N to background levels towards the end of July (Figures 4 and 6), meaning that N₂O emissions after this period are due to random variation in the soil and not associated with treatment effects.

N₂O emissions from soils are renowned for their high spatial and temporal variability (Flechar et al., 2007), which despite the intensive sampling regime and use of a large number of replicate static closed chambers in this experiment, may also have contributed

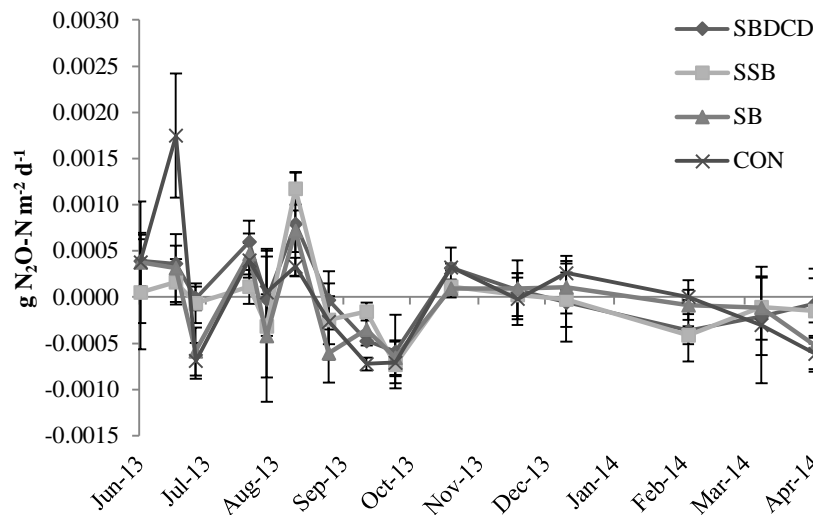
to large variation in N_2O emissions within treatments, thereby masking any treatment effects. Most of the events in which the soil acted as a sink for N_2O occurred in the period from July onwards (Figure 6). During this time the soil mineral N levels had returned to approximately their background levels and greater precipitation was recorded than had previously occurred in the experiment. These conditions are often associated with soils acting as an N_2O sink due to reduction of N_2O to N_2 during denitrification (Chapuis-Lardy et al., 2007).

Figure 4. Field daily GHG fluxes for each treatment over the experimental period **a)** N_2O fluxes during April 2013 and May 2013 **b)** N_2O fluxes from June 2013- April 2014 **c).** CH_4 fluxes during April 2013 and May 2013 **d)** CH_4 fluxes from June 2013- April 2014. **e).** CO_2 fluxes during April 2013 and May 2013 **f).** CO_2 fluxes from June 2013- April 2014

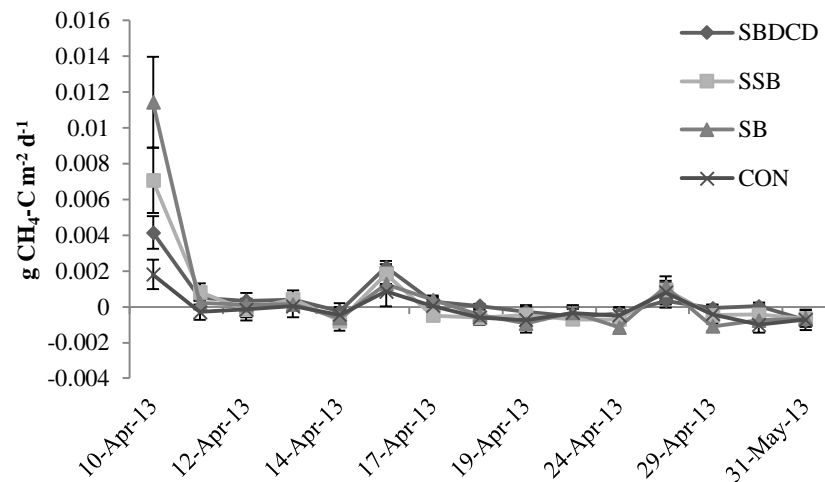
a).



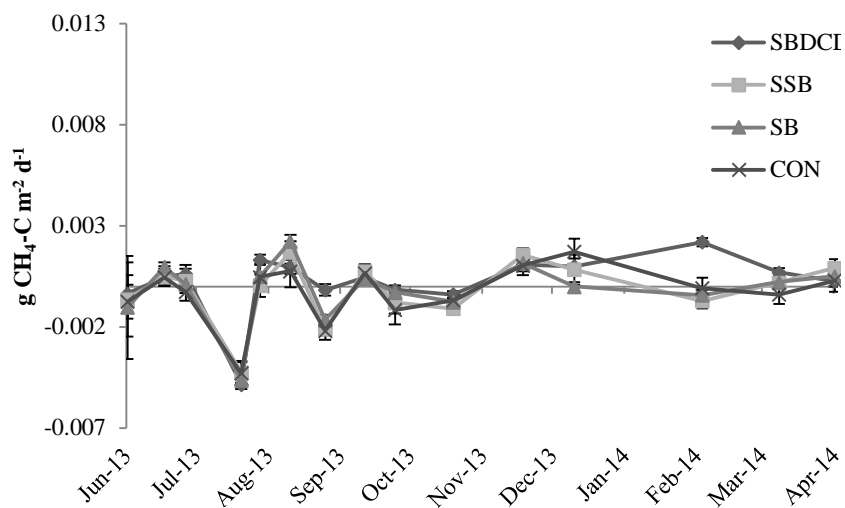
b).



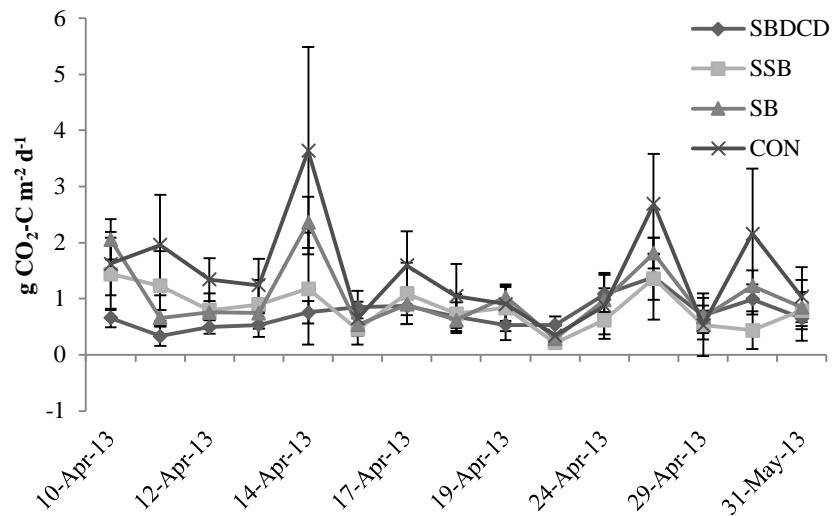
c).



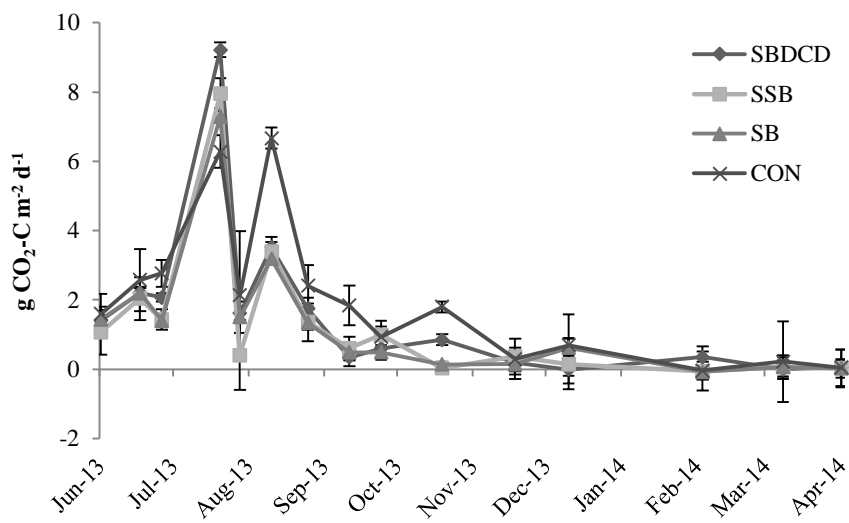
d).



e).



f).



CH₄ emissions were high on the day of fertiliser application (10th April 2013) for all treatments except the control, with maximum emissions of 0.011 g CH₄ m⁻² d⁻¹ from the SB treatment. By the following day emissions had decreased to < 0.0018 g CH₄ m⁻² d⁻¹, however small peaks in emissions did occur after this with a maximum of 0.0022 g CH₄ m⁻² d⁻¹ from the SB treatment on 9th August 2013. The soil frequently acted as a CH₄ sink with a minimum recorded value of -0.0046 g CH₄ m⁻² d⁻¹ from the SBDCD treatment on 29th July. Cumulative CH₄ emissions reflected the soil acting as a sink with negative cumulative emissions obtained for all treatments, however there were no significant treatment effects. Low soil moisture conditions, as were recorded throughout this experiment, are often associated with soil acting as a CH₄ sink due to the prevalence of methanotrophic bacteria. Methanotrophic bacteria metabolise and oxidise CH₄, resulting in the observation of a CH₄ sink effect (Johnson, 2007). The sink effect may explain why there was no significant difference between the treatments as the soil was acting as a greater sink for CH₄ emissions than a source, thereby concealing any emission effects associated with the treatments.

CO₂ emissions remained steady throughout most of the experiment with values < 4 g CO₂ m⁻² d⁻¹, except for peaks in emissions on 29th July and 19th August when the maximum daily emission of 9.22 g CO₂ m⁻² d⁻¹ was obtained from the SBDCD treatment. The greatest cumulative CO₂ emissions were from the CON treatment, with a value of 637 g CO₂ m⁻². The greater CO₂ emissions from the CON treatment are suggested to be due to possible differences in physical soil structural properties, for example, control soils may have been more aerated and less compacted from traffic associated with treatment application operations. Soils with better soil structure not only increase aeration and CO₂ emissions but also improve crop yields (Ball, 2013).

8.4 Conclusion

The results of this research indicated that the amendment of stored cattle slurry with oil seed rape straw biochar did not significantly affect GHG emissions. However, there were differences between the treatments with the biochar amended slurry initially acting as a sink for CO₂, unlike the “slurry only” treatment. The use of CO₂ during methanogenesis, possibly promoted by the additional labile C provided by the biochar, is suggested to be responsible for the sink effect. The “slurry + biochar” treatment also acted as a sink for N₂O more frequently than the “slurry only” treatment. This indicates that the higher pH of the “slurry + biochar” mixture may have promoted reduction of N₂O to N₂ during the denitrification pathway. The results of the field experiment demonstrated no significant effect of the biochar or nitrification inhibitor amendments on GHG emissions or crop yield. N₂O emissions from all treatments were minimal due to dry weather conditions inhibiting production of N₂O in the soil. This resulted in negligible differences in N₂O emissions between treatments. The lack of effect of the nitrification inhibitor on N₂O emissions, despite it increasing soil NH₄⁺ concentrations is suggested to be due to the low overall N₂O emissions, in addition to the reduced effectiveness of DCD when in high organic matter environments. The soil frequently acted as a CH₄ sink in all treatments, this also reflects the low soil moisture contents. CO₂ emissions from the control treatment were greater from all other treatments. The lowest crop yield was also obtained from the control treatment reflecting the lower amounts of mineral N in the soil as no fertiliser was applied. Further research is needed to assess the effect of biochar on GHG emissions from stored slurry over a longer timescale and from biochar amended slurry on alternative soil types and under different environmental conditions.

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Chapter 9.

Discussion

9. Discussion

9.1 Introduction

The overall aims of this thesis were to:

- a). Improve the understanding of processes and factors affecting N₂O emissions from arable agricultural soil, with a view to improving the accuracy of the UK's agricultural N₂O emission factors (EFs) and agricultural N₂O inventory.
- b). Investigate the effectiveness of potential N₂O mitigation options for arable agricultural soil, including the use of biochar.

This thesis sought to achieve these aims through the experimental work described in Chapters 5, 6, 7 and 8. The effect on N₂O emissions from an arable soil of applying varying rates and types of synthetic nitrogenous fertiliser were assessed through a year long field experiment described in Chapter 5. The potential of the nitrification inhibitor DCD to be used as an N₂O mitigation option was also explored. Chapter 6 investigated the effects of various types of organic fertilisers on N₂O emissions from an arable soil and whether altering the form of fertiliser, timing or method of application could decrease N₂O emissions. Chapters 7 and 8 were linked as Chapter 7 represented the preliminary experiment for the work described in Chapter 8. These chapters explored the potential for biochars to retain NH₄⁺ or NO₃⁻ and whether a selected biochar could be used to decrease N₂O emissions from stored slurry and slurry applied to an arable soil. The use of DCD was also investigated, to see whether N₂O mitigation effects would occur following DCD application to a slurry and biochar amended soil. The discussion chapter aims to address the main findings of the work described in Chapters 5, 6, 7 and 8 and the implications of these findings in relation to previous research described in the literature.

9.2 N₂O emissions from arable systems

Approximately 90 % of the UK's agricultural N₂O emissions originate from soils, making it vital that we thoroughly understand the production of N₂O from this source if we are to attempt to decrease N₂O emissions (Defra, 2011). The variety of factors which affect N₂O production in agricultural soils, including weather conditions, soil type, fertiliser type and application process, result in inevitable variation in the magnitude of N₂O emissions within a country. However, as a consequence of the lack of measured N₂O emissions from arable land, it is necessary for the UK to use the IPCC's default Tier 1 Emission Factor (EF₁) of 1.25 % (to be decreased to 1 % in 2015) across the entire country when reporting N₂O emissions for the UK's GHG inventory (IPCC, 2006). In areas such as Scotland where wetter and cooler weather is generally more prevalent than in the rest of the UK (Smith et al., 1998), N₂O emissions are likely to reflect these conditions. Annual cumulative N₂O emissions following application of synthetic N fertiliser to arable soil, as presented in Chapter 5, ranged from 1.32 to 3.82 kg N₂O ha⁻¹. Previous research has suggested that N₂O emissions from Scottish sites are generally small due to low temperatures limiting production of N₂O (Smith et al., 1998). However, N₂O emissions from our ammonium nitrate (AN) 120 kg N ha⁻¹ treatment were approximately four times greater than those reported by McTaggart et al. (1997) and Smith et al. (1998) for the same treatment applied in South East Scotland in 1993 and 1994-1995 respectively. Although the mean air temperature during our experimental period of April 2011- April 2012 was 9 °C, the same as the 30 year mean air temperature between 1971- 2000, the air temperature in the first four weeks following application, when the majority of emissions are suggested to occur (Bouwman, 1996) was 13 °C, which is likely to have promoted high N₂O emissions during this period (Smith et al., 2003).

Another contributory factor is the precipitation in our year of measurement which was approximately 150 mm greater than the 30 year mean of 676 mm. Analysis of soil

WFPS data and N₂O emissions in Chapter 5 determined a significant positive relationship between N₂O emissions and WFPS ($p < 0.001$), regardless of soil NO₃⁻ content, in contrast to previous research which has demonstrated that a threshold level of soil NO₃⁻ of 5 mg N kg⁻¹ is required before a relationship between N₂O emissions and WFPS is obtained (Clayton et al., 1997; Dobbie et al., 1999; Smith et al., 1998). WFPS also had considerable influence over the N₂O and NH₃ emissions reported following the application of organic fertiliser to arable soil (see Chapter 6). Large peaks in N₂O emissions after the autumn application, and overall greater N₂O emissions following autumn application than spring, were associated with increases in soil WFPS, in addition to higher soil temperatures in the autumn compared to the spring. This finding supported previous research which had also shown greater N₂O emissions from autumn applied organic fertiliser (Thorman et al., 2007) and effects of weather conditions on N₂O emissions following application of organic fertiliser (Clemens and Huschka, 2001; Shepherd and Newell-Price, 2013). Ammonia emissions were also dependent on environmental conditions, with the greater NH₃ emissions from the spring applied treatments suggested to be due to the drier weather conditions following spring application (Meisinger and Jokela, 2000). The apparent effects of soil temperature and WFPS on N₂O and NH₃ emissions during our years of measurement reflect the need to consider weather and soil conditions when applying fertiliser in order to minimise N₂O or NH₃ emissions. This will be particularly important in the future with predicted increases in temperature and precipitation across the UK increasing the risk of high emissions of N₂O from Scottish arable soils (Falloon et al., 2010; Met Office, 2012).

Chapter 5 forms part of a Defra project measuring agricultural N₂O emissions throughout the UK (described in Appendix 1). As such, it is possible to compare N₂O emissions from our Scottish site (Gilchriston, East Lothian, described in Chapter 5) to those sites in other areas of the UK (Rosemaund, Hereford and Woburn, Bedfordshire) to which comparable treatments were applied. This enables assessment of the effect of location on N₂O emissions, if only for the year of measurement. Weather conditions

over the measurement period varied considerably between the sites with almost twice the amount of rainfall recorded at Gilchriston (822 mm) in comparison to Rosemaund (418 mm) and Woburn (473 mm), despite similar 30 year average annual rainfall values (Bell et al., in prep.). Mean cumulative annual N₂O emissions also varied greatly between sites, with significant differences between emissions from all sites with the greatest mean annual cumulative N₂O emissions from Gilchriston (2451 g N₂O-N ha⁻¹), and emissions of 1571 g N₂O-N ha⁻¹ from Woburn and 935 g N₂O-N ha⁻¹ from Rosemaund. In contrast to the significantly lower N₂O emissions obtained from the AN 120 kg ha⁻¹ + DCD treatment at Gilchriston ($p < 0.05$), no significant N₂O mitigating effect was observed at the other sites in addition to no significant decreases in emissions from the urea treatments or split fertiliser application treatments (Bell et al., in prep.). Emissions were only measured for one year, thus meaning that it is difficult to determine the impact of climate on emissions or whether alternative factors may be responsible. However, the differences in rainfall appear to have been particularly influential on the recorded N₂O emissions. Soil WFPS was found to significantly influence N₂O emissions at Gilchriston and Rosemaund, demonstrating the considerable influence it has on N₂O production (Bell et al., in prep.).

Although it is important to understand the driving variables behind N₂O production and the differences in emissions between the sites, the ultimate aim of the ACO116 project was to improve the accuracy of the UK's agricultural N₂O inventory by determining whether the Tier 1 EF was appropriate for use across the UK. Given the significant differences in annual cumulative N₂O emissions between the sites it could be expected that there would also be significant differences in mean EFs between the sites. However, there was a large amount of variation in EFs for treatments at each site, meaning that there was no significant difference in EFs between the sites. The greatest mean EF was obtained for Gilchriston (0.69 %) compared to Rosemaund (0.18 %) and Woburn (0.39 %) (Bell et al., in prep.). These mean values are all below the new UK Tier 1 IPCC EF₁ of 1 % and only one treatment (the AN 120 kg N ha⁻¹ treatment from Gilchriston) from

all the sites exceeded the previous EF of 1.25 %. Although these results support the movement from the 1.25 % EF to the 1 % EF it suggests that perhaps the 1 % EF is still too high (Bell et al., in prep.; Halvorson and Del Grosso, 2013). However, as the EFs reported for these sites were only obtained based on a one year measurement period, it would be necessary to obtain measurements from a longer period and from other sites before a definite conclusion could be made. The lack of significant differences between EFs from the different sites indicates that the use of a default EF for the whole of the UK is appropriate. This is in agreement with Buckingham et al. (2014) who reported that 83 % of the UK's agricultural N₂O EFs were within the range of 0.03 % to 3 %, defined as the uncertainty boundary for the EF₁. Nevertheless, previous research has demonstrated the potential for large variation in agricultural N₂O EFs, with values > 30 % reported (Buckingham et al. 2014; Stehfast and Bowman, 2006), suggesting that the use of a single EF is not appropriate and demonstrating the requirement for further investigation into this issue.

The 1.25 % EF (or 1 % EF) is also used to calculate N₂O emissions from organic fertiliser applications to arable soil. EFs were calculated in Chapter 6 following the application of a range of organic fertilisers to arable soil. The mean N₂O EF for autumn and spring applied treatments combined was 0.65 %, which is lower than the default EF, however, the mean EF of 1.49 % for the autumn treatments was greater than the default EF whereas the mean EF was only 0.39 % for the spring treatments. The difference in EFs dependent on fertiliser application timing indicates that the use of a default EF regardless of application timing is inappropriate and that EFs used for inventory calculations should take into account the timing of fertiliser application. Again however, as this is only based on the results from a reasonably short period of measurements, more research would be needed to confirm or refute this suggestion. All of the autumn application treatments except the control produced significantly greater N₂O emissions compared with spring application treatments ($p < 0.05$), as a result of the drier environmental conditions experienced in the spring. There were no significant

differences in cumulative N₂O emissions within autumn applied treatments, or within spring applied treatments. The range of N₂O EFs obtained (-1.1 % to 2.78 %) were within the range of previously reported values (Chadwick et al., 2000; Velthof et al., 1992; Webb et al., 2014). Although there were no significant differences between treatments, the results supported previous research by Chadwick et al. (2011) which suggested that solid manures (such as FYM, poultry litter and layer manure in our experiment) often produce lower N₂O emissions and EFs as a result of their lower available N content, demonstrating the need for EFs to take into account the differences between organic fertiliser treatments.

The mean N₂O EF obtained for the synthetic fertiliser experiment (Chapter 5) of 0.69 % is very similar to the mean of the organic fertiliser experiment (Chapter 6) of 0.65 %. Although it is obviously difficult to compare these experiments as they were conducted at different sites, at different times and with different N application rates, this does appear to support the use of the same N₂O default EF for synthetic and organic fertiliser applications. However, when annual cumulative N₂O emissions are compared it is observed that the maximum cumulative N₂O emission from the synthetic fertiliser experiment was 3.82 kg N₂O-N ha⁻¹ from the AN 200 kg N ha⁻¹ application, compared to the organic experiment where the maximum cumulative annual N₂O emission was 2.91 kg N₂O-N ha⁻¹ from a larger application of 244 kg N ha⁻¹ from the layer manure treatment. The trend for generally greater emissions from synthetically fertilised soils in comparison to organically fertilised soils is in contrast to reviews of previous experiments which have demonstrated generally greater emissions from organic fertiliser in comparison to ammonium based synthetic fertiliser (Bouwman et al., 1996, 2002). However, this theory has been disputed and it is suggested that factors such as soil management may be more influential in determining N₂O production than fertiliser type (Mosier et al., 1996). The results obtained in Chapters 5 and 6 are likely to reflect the differences in site and climate, demonstrating the need for further research into potential differences between N₂O EFs following synthetic or organic fertiliser applications.

Chapter 6 also describes NH_3 EFs calculated for a range of organic fertiliser treatments. All of the calculated NH_3 EFs were lower than the default 20 % EF, however the mean spring EF of 15.5 % was over double that of the autumn treatments, reflecting the drier soil conditions following spring application which enhanced production of NH_3 (Meisinger and Jokela, 2000). The layer manure (LM) treatment produced significantly greater NH_3 emissions than all the other treatments following autumn and spring application. This was suggested to be due to the high dry matter content of the LM which decreased infiltration of the manure into the soil, thereby increasing the length of time over which NH_3 emissions took place, and also the high NH_4^+ content of the LM (Chambers et al., 1999; Menzi et al., 1997). The NH_3 EFs obtained suggest that the current default EF of 20 % is too high, however, previous research has demonstrated NH_3 EFs from spread animal manure of 20 – 30 % (Hutchings et al., 2000). It is clear that differences in NH_3 emissions exist based on differences between treatments and as such it is necessary for the default EFs to reflect this but as this work has shown, NH_3 EFs are highly variable and difficult to predict.

Sustainable intensification of agriculture is being viewed as a solution to the pressing issues of an increasing global population coupled with a rise in demand for food production (Garnett et al., 2013). Increasing fertiliser applications may be seen as a way in which we may increase crop production, however, if production is to be sustainable then consideration not only of crop yields but also of GHG production must also be taken into account, making measurement of yield scaled emissions a vital area of research for the future. Despite the value of measuring yield scaled emissions, instead of just N_2O emissions, these are not commonly described in the literature. Crop yield at Gilchriston (Chapter 5) generally increased with increasing rates of fertiliser application, an effect which was also observed at Woburn (Bell et al., in prep.). However, significantly greater yield scaled emissions were obtained at Gilchriston in comparison to Woburn and Rosemaund ($p < 0.05$), reflecting the higher N_2O emissions obtained at Gilchriston. The maximum crop yield obtained for the synthetic fertiliser experiment

(Chapter 5) of 9.3 tons ha⁻¹ was almost double that obtained in the organic fertiliser experiment (Chapter 6). Although it is difficult to compare these experiments, these findings demonstrate the potential issues with organic fertilisers related to difficulties in accurately timing the availability of the nitrogen to correspond with crop demand. This is due to organic fertilisers containing a combination of “readily available” N which is immediately available for plant uptake, and organic N which needs mineralising to plant available forms over time, unlike synthetic fertiliser such as AN where all of the N is available for plant uptake immediately (Defra, 2010). Although N₂O emissions from the organic fertiliser experiment were generally lower than from the synthetic fertiliser experiment (possibly due to late sowing and birds eating the crop at the organic site), the lower crop yields from the organic fertiliser resulted in mean yield scaled N₂O emissions of 3.86 kg N₂O-N ton⁻¹ grain compared to 0.31 kg N₂O-N ton⁻¹ grain from the synthetic fertiliser. As previously mentioned, yield scaled N₂O emissions are an area which must be carefully considered when implementing N₂O mitigation options or choosing whether to apply synthetic or organic fertiliser.

The high spatial and temporal variability of N₂O emissions makes them challenging to measure in the field environment. The experiments described in Chapters 5, 6 and 8 attempted to overcome these challenges by using a large number (15) of static closed chambers per treatment in contrast to previous experiments which have often used < 6 chambers per treatment (Dobbie and Smith, 2003; Smith et al., 2012). However, a large amount of variation in emissions within treatments was still obtained, often resulting in a lack of significant differences between treatments. It appears that a greater number of chambers may have been necessary, however, due to time and resource constraints this would have been challenging to achieve. The use of automatic N₂O measurement chambers could be a useful way of overcoming the challenges surrounding temporal variation in emissions, however to also overcome the spatial variability issues a large number of automatic chambers would be required which would be unfeasible due to the high costs involved. As has been mentioned previously, the time period over which

experiments take place is crucial when assessing the effect of climate on emissions. Due to limited time and resources the experiments described in this thesis could not be longer than a year each, however, ideally experiments would continue for at least two years, in order to assess the effect of climate on emissions. Additionally, it would also be ideal to measure emissions of not only N_2O but also NH_3 and leaching losses of N in order to thoroughly understand N loss pathways. Measurement of CO_2 and CH_4 should also be conducted so that a complete GHG budget could be created for each treatment and to ensure that trade offs between emissions are not occurring.

9.3 Mitigation of N₂O emissions from arable soil

The analysis of N₂O emissions following the application of synthetic fertiliser to arable soil (Chapter 5) demonstrated the importance of synthetic fertiliser application rate in determining N₂O emissions. Nitrous oxide emissions generally increased with increasing rates of AN fertiliser application with cumulative annual emissions ranging from 1.66 kg N₂O-N ha⁻¹ from the Control treatment to 3.82 kg N₂O-N ha⁻¹ from the 200 kg N ha⁻¹ AN treatment. The strong linear relationship obtained between the amount of fertiliser applied and the cumulative annual N₂O emissions ($p < 0.001$) demonstrates the harmful consequences of over fertilising soils, in terms of potential increases in GHG emissions. A linear relationship between N₂O emissions and fertiliser application rate, in contrast to an exponential relationship as has been described by Hoben et al. (2011) and McSwiney and Robertson (2005), also confirms the IPCC's EF calculation approach which assumes that N₂O emissions are a linear function of N application (Philibert et al., 2012). These findings reflect the need for good understanding of crop N demand and application of appropriate rates of N fertiliser and suggests that different EFs dependent on the rate of fertiliser application are not required.

Although fertiliser application rate is influential in determining the magnitude of N₂O emissions, the type of synthetic fertiliser applied is also important. The urea fertiliser treatment used in the work described in Chapter 5, was applied at the same rate as the 120 kg N ha⁻¹ AN treatment, but produced 26 % lower N₂O emissions, supporting the previous findings of Dobbie and Smith (2003) and Smith et al. (2012). However, urea [CO(NH₂)₂] is highly susceptible to decomposition into NH₄⁺ when in the soil and subsequent volatilization into NH₃ (Pierzynski et al., 2005). Approximately 22 % of urea N is emitted as NH₃ following application to arable soil, in contrast to < 3 % of ammonium nitrate N (Smith et al., 2012). It is likely that the lower N₂O emissions associated with the urea treatment are due to larger NH₃ emissions, therefore depleting the N source in the soil. However, it has been demonstrated that when the loss of N as

NH₃ following urea applications is taken into account, the difference between N₂O lost as a % of fertiliser N for urea and AN fertiliser is much smaller (Smith et al., 2012). The differences in measured N₂O emissions and expected NH₃ emissions between these treatments reflects the potential for N emission tradeoffs to occur.

Tradeoffs between N₂O and NH₃ were also evident from the results of the organic fertiliser experiment described in Chapter 6. N₂O emissions were generally smaller than NH₃ emissions, with mean N₂O emissions as a % of N applied of 1 % in comparison to mean NH₃ emissions as a % of N applied of 11 %. However, when N₂O and NH₃ emissions from the autumn applied treatments are compared to those from the spring applied treatments, the issue of trade offs is noticeable. Greater N₂O emissions were released from the autumn applied treatments compared to the spring applied treatments, however greater NH₃ emissions were produced from the spring applied treatments than the autumn applied treatments. The lack of incorporation of the spring applied treatments may have enhanced the production of NH₃, and the dry spring weather conditions may also have contributed to NH₃ production (Wulf et al., 2001). This makes trade offs between the emissions of both gases almost inevitable, although other contributory factors such as crop growth rate and uptake of N must also be considered. Although loss of N via leaching wasn't measured as part of this thesis, this is another N loss pathway which must also be considered, with greater leaching losses of N likely in wet soil conditions and up to 30 % of N potentially lost via leaching following fertiliser application (IPCC, 2006).

Both N₂O and NH₃ are environmentally harmful gases, but as previously mentioned it may be difficult to decrease emissions of both simultaneously. Although NH₃ may cause environmental impacts such as eutrophication, if preventing climate change is the main priority then mitigation of N₂O should be focused on. Despite mean NH₃ emissions recorded in Chapter 6 that were 11 times greater than those of N₂O, indirect N₂O

emissions associated with emissions of NH_3 only account for 1 % of the NH_3 emitted, which in this case would represent 0.11 % of applied N fertiliser, considerably smaller than the 1 % of applied N fertiliser emitted as N_2O .

The timing of organic fertiliser application was evidently important in determining N_2O emissions. Consideration of fertiliser application timing is a simple no cost yet effective N_2O mitigation procedure that farmers could adopt if given adequate advice and recommendations for their soils. The form of organic fertiliser that is applied is another simple mitigation option that the results of Chapter 6 demonstrated could be a practical method for farmers to decrease emissions of either N_2O or NH_3 . However, as previously mentioned, it becomes more challenging when attempting to decrease emissions of both gases simultaneously. Also, use of locally sourced fertilisers reduces fossil fuel CO_2 emissions associated with transporting fertilisers from another part of the country. Although there were no significant differences between cumulative emissions of N_2O within the autumn applied treatments and within the spring applied treatments, there were noticeable differences in emissions associated with fertiliser properties such as moisture content. The large N_2O emissions from the autumn applied slurry treatments were possibly due to the high moisture content of the slurry, enhancing localised soil moisture content and thereby increasing denitrification rates (Davidson, 1992). Moisture content was also an important factor controlling NH_3 emissions with high emissions from the layer manure and poultry litter, both of which had high dry matter contents (Chambers et al., 1999). Choosing an appropriate fertiliser to decrease N_2O or NH_3 emissions may be a mitigation option which farmers could sustainably carry out, however, other considerations such as the local availability of a chosen fertiliser would also be important.

The method of organic fertiliser application has previously been demonstrated to have the potential to decrease emissions, with lower emissions reported from broadcast

slurry compared to surface broadcast slurry (Webb et al., 2010). However, this was not evident in our results possibly due to the slurry for both treatments remaining on the surface of the soil for the same amount of time. This is another simple potential N₂O mitigation option that farmers could adopt, however, tradeoffs between emissions of N₂O and NH₃ must again be carefully considered and further research into application and incorporation methods is needed.

Split applications of N fertiliser is another potential N₂O mitigation option which was considered in Chapter 5. However, although there was a decrease in N₂O emissions of 11 % associated with the AN fertiliser being applied in 3 doses instead of 2, which may indicate an increase in N use efficiency, there was no significant difference in crop yield or grain or straw N contents between the treatments. This suggests that the 3 split application treatment was not an effective N₂O mitigation option, at least for the arable site studied here. Although previous research has demonstrated the N₂O mitigation potential of split fertiliser applications (Burton et al., 2008), this option must be carefully assessed due to issues such as increased soil compaction which may result from additional fertiliser applications, potentially promoting N₂O production (Ball, 2013).

The use of nitrification inhibitors such as dicyandiamide (DCD) have been proven to successfully inhibit the production of N₂O (Di and Cameron, 2003; Di et al., 2007). However, the majority of research involving DCD has taken place on grasslands rather than arable land, and there has been very little research into its potential as an N₂O mitigation option in the UK, especially in Scotland. Chapter 5 demonstrated the significant decrease in N₂O emissions associated with the use of DCD following application of AN fertiliser ($p < 0.05$). It was also found that DCD decreased N₂O emissions following application of urea fertiliser but this was not significant. Previous research has demonstrated greater effectiveness of DCD when applied with urea than AN (McTaggart et al., 1997). However, it may be that greater NH₃ emissions were

produced from the urea treatments in our study thereby depleting the NH_4^+ pool, meaning that the majority of N_2O may have been produced by the denitrification pathway thus making the DCD less effective. Research into the effectiveness of DCD when applied with organic fertilisers has produced mixed results (Merino et al., 2001, 2002; Mkhabela, 2006; Vallejo et al., 2005), hence the need for further research into this area. As such we applied DCD following the application of a slurry and biochar mixture to arable soil (see Chapter 8). There was no effect on N_2O emissions of the DCD amended treatment compared to the non amended treatment. This was suggested to be due to decreased effectiveness of DCD in high organic matter environments, possibly due to sorption of DCD to the organic matter (Slangen and Keerhoff, 1984). Additionally, N_2O emissions were particularly low in Chapter 8, with cumulative annual N_2O emissions from the biochar and slurry treatment (unamended with DCD) of $-0.0035 \text{ g N}_2\text{O-N m}^{-2}$, in comparison to $0.33 \text{ g N}_2\text{O-N m}^{-2}$ from the unamended AN 120 kg N ha^{-1} treatment from Chapter 5. The very low production of N_2O means that any effect of the DCD on emissions would likely be negligible.

Research into the effects of DCD on N_2O emissions have also frequently reported increased crop yields (Di and Cameron, 2002; Liu et al., 2013; Pain et al., 1994). In contrast to this we found significantly decreased spring barley crop yields associated with the AN 120 kg ha^{-1} + DCD treatment and UR 120 kg ha^{-1} + DCD treatment from Chapter 5, but no decrease in winter wheat yields associated with the amendment of the slurry and biochar application with DCD in Chapter 8. It has been suggested that plants may preferentially uptake NO_3^- from the soil due to greater ease of transport of NO_3^- through the soil compared with NH_4^+ which is more tightly bound to the soil particles (Hofman and van Cleemput, 2004). If the DCD prevents conversion of NH_4^+ to NO_3^- by nitrification, as was evident in Chapter 5, then crop N uptake and growth may suffer, although this has not been reported previously for grassland (Di and Cameron, 2002). There were no significant differences between grain and straw N contents for the DCD amended and unamended treatments in Chapter 5 or Chapter 8. This raises questions

about how DCD affects crop yield and particularly why different effects were observed following synthetic and organic fertiliser applications. The potential for DCD residues to contaminate crop products must also be considered before widespread usage, following recent concerns regarding the toxicity of DCD found in milk powder produced by cows grazing on DCD amended grassland in New Zealand (Lucas, 2013).

9.4 The potential for biochar to be used as a N₂O mitigation option

One of the mechanisms which has been suggested to account for observed decreases in N₂O emissions following biochar amendment of soil is the retention of NH₄⁺ and NO₃⁻ by the biochar, rendering these forms of N unavailable to soil microbes (Clough and Condron, 2010). The work described in Chapter 7 aimed to confirm whether retention of NH₄⁺ and NO₃⁻ was taking place, and if so, to select the biochar with the greatest N retention capacity for use in the slurry storage and application experiment described in Chapter 8. The results of Chapter 7 indicated that all of the 6 biochars tested were able to retain both NH₄⁺ and NO₃⁻ as shown by decreased solution concentrations of NH₄⁺ and NO₃⁻ following the mixing with, and then removal of, biochar. Retention of NO₃⁻ by biochar has not been described as frequently in the literature as retention of NH₄⁺, and although NO₃⁻ retention was observed in Chapter 7, greater retention of NH₄⁺ occurred, supporting the results obtained by Hollister et al. (2013) and Yao et al. (2012). The generally net negative surface charge of biochars produces a high cation exchange capacity, thereby promoting retention of cations such as NH₄⁺ (Cheng et al. 2006). NO₃⁻ is likely to be held in solution in biochar pores or through anion exchange and therefore the magnitude of NO₃⁻ sorption is expected to be smaller (Kameyama, 2012; Prendergast-Miller et al., 2011). During pyrolysis of biochar the majority of N is volatilized (Shackley and Sohi, 2010), however small amounts of N may remain and these may be released as was observed in Chapter 7. Previous research has demonstrated increased crop yield following application of biochar, potentially due to release of nutrients from the biochar and/or retention of nutrients within the soil by the biochar (Chan et al. 2007; Major et al. 2010; Mukherjee and Zimmerman, 2013). However, no crop growth effects, either positive or negative, were observed following biochar application to the field in Chapter 8. Ideally the effect of biochar on crop yield would have been measured for a few years, as research has demonstrated that positive effects of biochar on crop yield may occur over longer periods of time due to impacts of biochar on crop rooting and soil water (Jones et al., 2012).

Of particular interest to field experiments is the capacity of biochar to retain N due to the potential N₂O mitigation effects. The results of Chapter 7 indicated that biochar N retention reaches a limit or saturation point, as the % of the initial concentration of the sorbate which was removed by the biochar as NH₄⁺ or NO₃⁻ decreased as the concentration of the sorbate increased. An area of biochar research of particular interest to agricultural research is the potential to create biochars which have been designed for a specific purpose e.g. with the maximum ability to retain N. As such, Chapter 7 aimed to elucidate the properties of the biochar which affected N retention. The effect of biochar particle size on N retention was investigated through the use of biochar of two particle sizes (<1 mm and 1-4 mm), however no particle size effects on N retention were observed. Although external surface area, as controlled by particle size, does not appear to influence N retention, previous work has suggested that the internal surface area of biochar i.e. nanoporosity may be more important (Hale et al., 2011; Zheng et al., 2010). Previous research has demonstrated a decrease in CEC as pyrolysis temperature increases (Cheng et al., 2006; Nguyen and Lehmann, 2009) and this was supported by Chapter 7, with significantly decreased NH₄⁺ retention as pyrolysis temperature increased (p<0.05). The lack of effect of pyrolysis temperature on NO₃⁻ retention reflects the different mechanisms responsible for NH₄⁺ and NO₃⁻ retention. Biochar pH was also expected to affect CEC, with increased pH increasing CEC (Silber et al., 2010), however, no pH effect was observed.

The high NH₄⁺ and NO₃⁻ retention capacity of the oil seed rape straw biochar (Chapter 7) were the basis for its use in the experiment described in Chapter 8. At this point it was known that the biochar had the potential to retain NH₄⁺ and NO₃⁻ from solution. However, it remained unknown whether the retained NH₄⁺ and NO₃⁻ would be unavailable to microbes, potentially decreasing production of N₂O by nitrification or denitrification, and equally as important, whether the NH₄⁺ and NO₃⁻ would still be available for plant uptake. Following the storage of biochar with slurry in tanks in Chapter 8, no significant effects on GHG production from the slurry were observed, in

contrast to a smaller scale experiment by Angst et al. (2013). However, differences in GHG production between the treatments were observed. The treatment amended with biochar was generally observed to act as a stronger sink for N_2O than the slurry only treatment. It could be that this effect was due to retention of NH_4^+ and NO_3^- in the slurry by the biochar, as would be supported by the significant decrease in NH_4^+ and NO_3^- content of the slurry following storage with the biochar. However, it would be expected that retention of N by the biochar would decrease N_2O emissions instead of causing the slurry to act as an N_2O sink. Even if retention of NH_4^+ and NO_3^- did occur, it appears as though the N was still available to nitrifiers and denitrifiers within the slurry due to the lack of significant N_2O mitigating effect observed. For the biochar and slurry mixture to act as an N_2O sink, N_2O must be consumed. A more likely explanation for this is the increase in slurry pH which was observed over the experimental period, as this would increase the reduction of N_2O to N_2 during denitrification (Chapuis and Lardy, 2007). The biochar amended slurry also initially acted as a sink for CO_2 , in contrast to the unamended slurry and this was suggested to be due to labile C in the biochar promoting methanogenesis, which would also account for greater initial production of CH_4 in the biochar amended treatment.

Chapter 8 also describes the results of applying the contents of the slurry tanks to the field. The results of this experiment indicated that there were no significant effects of the biochar on GHG production. It was hypothesised that the biochar may retain N from the slurry whilst in the slurry tanks, thereby decreasing availability of N when the slurry and biochar mixture was applied to the soil and subsequently decreasing N_2O production. The lack of N_2O mitigation observed following application of the biochar and slurry mixture to the soil, in comparison to the slurry only treatment, indicates that even if retention of NH_4^+ and NO_3^- by the biochar had occurred, the N was still available for N_2O production, and also for crop growth as mentioned earlier. The generally high cation exchange capacity of biochars means that when biochar is added to slurry or soil, it is likely to alter the cation exchange capacity of these substances which may affect

retention of nutrients. Cation exchange capacity of the biochar, and the slurry and soil to which it was added was not measured in this thesis due to time and resource constraints. However, it is suggested that if this had been done then perhaps it could have been known whether the amount of biochar applied to the slurry and soil was sufficient to substantially alter the cation exchange capacities of these and to influence N sorption and N₂O production. The results obtained regarding N₂O emissions from biochar amended soil are in contrast to previous field studies which have observed N₂O mitigating effects (Felber et al., 2014; Liu et al., 2012; Taghizadeh-Toosi et al., 2011). However, lower application rates of biochar were used in our experiment which will have decreased any influence of biochar on N₂O emissions. Weather conditions during the experimental period were very dry, with a mean soil WFPS of 40 %, well below the range at which maximum N₂O production is expected to occur at 50 – 70 % WFPS (Flechard et al., 2007). The lack of production of N₂O and the subsequent low N₂O fluxes obtained from all treatments imply that any N₂O mitigating effects of the biochar treatment may have been difficult to observe. Ideally, any future similar experiments should take place over a time period of a few years to take into account variability in weather conditions and should investigate a range of biochar application rates.

The results of the work described in Chapters 7 and 8 have significantly contributed to knowledge surrounding the potential for biochar to be used as a N₂O mitigation option. Based on the results of Chapter 7, it can be said with certainty that biochar from a range of feedstocks is able to retain NH₄⁺ and to a lesser extent, NO₃⁻. It would be expected that this N retention effect would also occur when biochar is placed into an environment with large quantities of N, such as slurry tanks or an N fertilised field environment. It is difficult to know whether N retention did take place following mixing of biochar into the slurry tanks, however, it appears likely that the differences observed in GHG emissions from the biochar amended slurry were due to physical properties of the biochar such as ash content which affects pH, as also observed by Angst et al. (2013). The additional lack of impact on N₂O emissions and crop yield of the slurry and biochar mixture when

compared to the slurry only mixture following application to the field indicates that any N retained by the biochar is still available to nitrifiers and denitrifiers and also for crop uptake. The results of this research suggest that a considerable amount of future work is still needed to assess the potential of biochar as an N₂O mitigation option. The differences in biochar properties which are dependent on factors such as feedstock material and pyrolysis temperature mean that it is not possible to say that the lack of N₂O mitigating effects observed following use of a particular biochar indicates that other biochars will also be unsuccessful. The potential for biochar to be used as a N₂O mitigation option firstly depends on elucidating the mechanisms responsible for previously observed N₂O mitigating effects, and secondly, selecting or “designing” biochars with the properties responsible for this. Although the application of biochar to soil undoubtedly has benefits for carbon sequestration (Ahmed et al., 2012), it appears as though its use as a GHG mitigation tool will be limited until the aforementioned goals have been achieved.

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Chapter 10.

Conclusions and recommended future work

10. Conclusions and recommended future work

10.1 Conclusions

The work described in this thesis has made a substantial contribution to the understanding of the processes and factors affecting N₂O emissions from arable soil and the effectiveness of potential N₂O mitigation options. Chapters 5 and 6 demonstrated the influence of climatic conditions, particularly soil WFPS and temperature, on the magnitude of N₂O emissions. It was observed that there was a significant positive relationship between soil N₂O emissions and WFPS, regardless of soil NO₃⁻ concentrations. Chapter 6 also illustrated the effect of climatic conditions on the tradeoffs between N₂O and NH₃ production. Greater N₂O emissions were observed following autumn application of organic fertiliser, however greater NH₃ emissions were observed following spring application. These tradeoffs were associated with higher soil WFPS and temperatures in the autumn but drier soil conditions and lack of incorporation of the fertiliser in the spring. The effects of soil WFPS and temperature on N₂O emissions are particularly important due to predicted future changes in the climate, increasing the risk of greater emissions of N₂O. The importance of assessing yield scaled N₂O emissions was evident in Chapters 5 and 6 and it is suggested that yield scaled emissions should be reported more frequently in the literature, particularly with the drive towards sustainable intensification.

A linear relationship between the application rate of synthetic fertiliser and N₂O emissions was observed in Chapter 5, supporting the use of a single EF for different application rates of synthetic fertiliser. The mean EF of 0.69 % obtained in Chapter 5, in addition to the lower mean EFs obtained in similar experiments as part of the Defra project (described in Appendix 1) supports the movement of the UK's Tier 1 EF from 1.25 % to 1 % in 2015, and suggests that perhaps the 1 % EF is too high. The cumulative N₂O emissions reported in Chapter 5 were greater than those reported from the

comparable Defra sites in England, reflecting the greater rainfall received at the Scottish site. However, there were no significant differences in the EFs between the sites indicating that the use of a single default EF value across the UK is appropriate. However, the variation in agricultural N₂O EFs which have been previously reported demonstrate the need for further research and the difficulties in relying on data obtained over only a one year period. The EFs reported in Chapter 6 following organic fertiliser application reflect the need for EFs to take into account fertiliser application season and fertiliser type, in addition to the potential need to decrease the default NH₃ EF. The EFs reported in Chapter 6 will be compared to the data reported from the other Defra experimental sites in the UK, once this becomes available, to determine whether trends in data are common across the sites. The EFs obtained in Chapters 5 and 6 will influence the future of the UK's EF calculations and the accuracy of the UK's agricultural N₂O inventory.

This thesis investigated various potential N₂O mitigation options. Based on findings outlined in Chapters 5 and 6, it was evident that the type of fertiliser applied influences N₂O emissions; however the importance of also taking into account tradeoffs between N₂O and NH₃ emissions was apparent. The use of split synthetic fertiliser applications and the method of organic fertiliser application did not significantly affect N₂O emissions, however, these have previously been reported to mitigate N₂O emissions and as such require further investigation under different soil and climatic conditions. The use of the nitrification inhibitor DCD was investigated in Chapters 5 and 8. Although there was a significant decrease in N₂O emissions reported when ammonium nitrate applications were amended with DCD, there was no effect when urea, or slurry and biochar applications were amended. The significant decrease in spring barley crop yields (by approximately 10 %) associated with the use of DCD with synthetic fertilisers described in Chapter 5 is concerning as it is vital to maintain crop yields whilst decreasing N₂O emissions. However, no winter wheat crop yield effect related to the use of DCD with slurry was observed (Chapter 8). The research into DCD in this thesis

makes a significant contribution to the body of research into the effectiveness of DCD use on arable soils with synthetic and organic fertilisers. However the contradictory results obtained reflect the lack of understanding surrounding the potential for DCD to be used as an N₂O mitigation option. The adoption of N₂O mitigation options by farmers is likely to depend on the ease of use of the option and financial considerations. Therefore simple options such as adjusting fertiliser application timing to take into account the weather conditions are likely to be popular, in contrast to options such as the use of DCD which as yet remains uncertain, especially in regard to issues associated with potential toxicity to humans.

The use of biochar as a potential N₂O mitigation option was also investigated in this thesis. The results presented in Chapter 7 demonstrated that a range of biochars were able to retain NH₄⁺ and NO₃⁻ from a solution, and that greater quantities of NH₄⁺ than NO₃⁻ were retained, reflecting the different retention mechanisms. Investigation into the properties of the biochars which affect N retention rates demonstrated a significant negative relationship between biochar pyrolysis temperature and NH₄⁺ sorption, related to pyrolysis temperature effects on CEC. There were no effects of biochar particle size or pH on either NH₄⁺ or NO₃⁻ retention. The N retention abilities of the biochar described in Chapter 7 indicated that the retention of N by biochar may be the mechanism responsible for decreased N₂O emissions observed in previous experiments. However, there were no significant decreases in slurry tank N₂O, CH₄ or CO₂ emissions when oil seed rape straw biochar was stored with slurry (Chapter 8), although the increased slurry pH associated with biochar addition may have caused the slurry to initially act as an N₂O sink. Following the application of the biochar and slurry mixture to the field, no N₂O mitigating effects of the biochar, or crop yield effects, were observed. The results of the work described in Chapters 7 and 8 demonstrated that biochar has the ability to retain NH₄⁺ and NO₃⁻, however, if this took place in the slurry tanks and in the field then any retained N was still available for production of N₂O and crop uptake as is evident from the lack of significant N₂O or crop yield effects. It is

suggested that the N₂O mitigating effects of biochar as observed in previous work may be due to a combination of factors, dependent on biochar properties or the reaction environment. At present it appears as though the amendment of soil with biochar has benefits for soil carbon sequestration but that its use for N₂O mitigation requires greater investigation.

10.2 Recommended future work

- Although differences in N₂O emissions between the Scottish site investigated in Chapter 5 and the corresponding Defra sites in England were reported, it is difficult to separate the effects of climate from any other influences when the experiment is only conducted over a one year period. Ideally future work should take this into consideration and experiments should be conducted over a longer period of time. The use of a greater number of chambers per treatment than were used in this thesis may also be necessary to take into account the spatial and temporal variability of emissions and the use of a greater number of automatic N₂O measurement chambers would be preferred. In terms of assessing an overall GHG budget and partitioning the loss of N from different pathways, measurements of CO₂, CH₄, NH₃ and N leaching should take place in addition to N₂O. However, carrying out all of these suggestions may be limited by time and financial constraints.
- It is suggested that all future field experiments which measure N₂O should also measure yield scaled emissions. If farmers are to be encouraged to adopt practices that decrease N₂O emissions, information regarding crop yield will be vital.
- Previous work investigating the effectiveness of DCD in decreasing N₂O emissions from arable soil has been limited. The contradictory results of different chapters in this thesis regarding the effect of DCD on N₂O emissions and crop yield indicates that its effectiveness may be influenced by factors such as fertiliser type, crop variety, weather and soil conditions. Future research into DCD should investigate factors that control the efficacy of DCD in arable systems.
- The results obtained in this thesis regarding the potential N retention mechanism by which biochar may decrease N₂O emissions reflects the need for further research into the biochar properties which affect N retention. Biochar properties

including internal surface area, feedstock type, ash content, ageing of reactive functional groups and elemental content must be investigated.

- The application of biochar to soil should be focused on applying biochars which have those properties expected to cause decreased N₂O emissions. The application of biochar to field experiments therefore should firstly depend on identifying the mechanisms responsible for decreasing N₂O emissions. The use of a ¹⁵N labelled N source when biochar is used in field experiments could also help to determine the pathway by which N₂O emissions are potentially being decreased.
- The adoption of N₂O mitigation options such as DCD or biochar are going to ultimately depend on any impacts on human health associated with their use. The recent contamination of milk powders from New Zealand with DCD and subsequent concerns for human health indicate that research is needed in arable systems to assess whether residues of DCD can be found in grain following DCD application to the soil. It is known that biochar may contain heavy metals, polycyclic aromatic hydrocarbons and dioxins, all of which are harmful to humans and the environment. Additionally, the growth of various harmful fungi on the biochar in the experiment described in Appendix 3, indicates that research into any harmful effects associated with application of biochar to soil is required.

Appendix 1. Overview of the UK's Agricultural GHG Research Platform

The Agricultural Greenhouse Gas Research Platform is a large government funded research programme in the UK investigating agricultural GHG emissions (N₂O and CH₄). The aims of the N₂O research are to:

- Improve understanding of the factors controlling N₂O emissions from agricultural soils.
- Improve the UK's national greenhouse gas (GHG) inventory through a more accurate assessment of agricultural N₂O emissions.
- Produce emission factors (EFs) that take into account the range of soils, climate, crop and soil management within the UK.
- Move towards the IPCC Tier 2 approach to EF calculation.
- Investigate GHG mitigation options including: The use of nitrification inhibitors, the effects of timing of fertiliser application, and amounts of manufactured and organic nitrogen fertilisers on N₂O emissions.

The results of this research will provide evidence for the Department for Environment, Food and Rural Affairs, Welsh Assembly Government, Scottish Government, and the Department of Agriculture and Rural Development in Northern Ireland, to aid in creating policies which will decrease agricultural GHG emissions. This research will also help farmers to implement farming methods which will decrease GHG emissions but maintain crop productivity.

There are five phases of the N₂O research. These are:

1. Prioritisation phase

This aimed to identify the main soil and climatic zones of interest, and the main sources of N₂O which would be investigated. Standard experimental protocols were designed.

2. Measurements of direct and indirect N₂O emissions

Emissions were measured at 9 arable and grassland sites across the UK using static closed chambers. These sites represented the main soil and climatic regions used for agriculture in the UK and are shown in Figure 1. Sources of N under investigation included: N fertilisers, manures, and dung and urine deposition. Mitigation options which required investigation as identified through gap analysis included: the effect on N₂O emissions of fertiliser types, rates and application timings and the use of nitrification inhibitors.

3. Identification of proxies

The use of proxies such as soil wetness and soil mineral N content were assessed for their usefulness in identifying the impact of changes e.g. in soil conditions and agricultural practices, on N₂O emissions.

4. Modelling

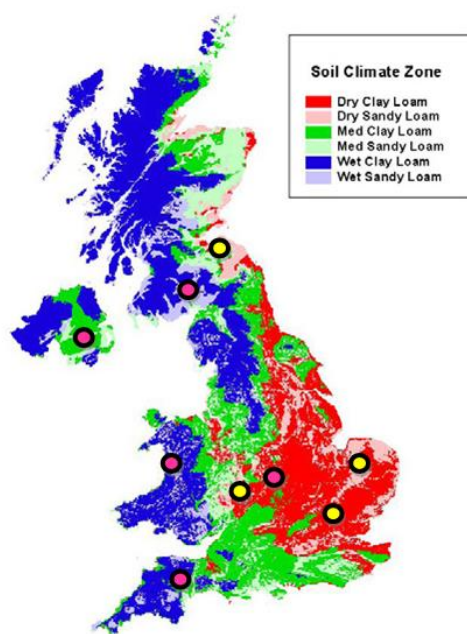
Modelling was used to interpolate missing data. Modelling was used to estimate Tier 2 and Tier 3 emission factors.

5. Verification of N₂O emissions

Verification of the measured and modelled N₂O emissions took place by comparing results of measured emissions using static closed chambers to e.g. automated chambers and eddy covariance techniques.

Further information is available at: [**http://www.ghgplatform.org.uk/**](http://www.ghgplatform.org.uk/)

Figure 1. *Location of the experimental sites. Arable sites are shown in yellow, grassland sites in pink.*



Appendix 2: Method development: Investigating the effect of headspace mixing using fans on measured N₂O emissions from static closed chambers

Introduction

Static closed chambers such as those used for sampling N₂O emissions from soils usually do not include a mechanism for continuous headspace mixing and N₂O is generally sampled manually from the headspace (Christiansen et al., 2011). When a closed chamber which does not use headspace mixing is placed on soil this can lead to the development of a gas concentration gradient within the headspace, subsequently resulting in underestimation of the actual gas flux when samples are taken from the top of the chamber. In addition to the development of a headspace concentration gradient, the procedure of manual sampling in an unmixed chamber can cause depressurisation of the chamber headspace resulting in mass flow of gas into the headspace from the soil to compensate for this effect (Bekku et al., 1995). The effect of headspace mixing (or lack of it) is particularly important in tall chambers which have a high minimum detectable flux (Rochette and Eriksen-Hamel, 2008) and which may not allow sufficient mixing of headspace air to take place (Rochette, 2011). Research into the effects on measured CO₂ and CH₄ fluxes from large static closed chambers (>60 L volume) has demonstrated that fluxes are underestimated when mixing of the headspace air does not take place (Rochette and Hutchinson, 2005; Christiansen et al., 2011). However, the volume of these chambers is greater than those generally used for N₂O sampling (approximately 35 L volume) and so headspace mixing may have affected measured fluxes differently.

The current guidance on best practice for static closed chamber design is uncertain when considering the mixing of headspace air within static closed chambers during measurement of N₂O emissions. Many researchers do not currently use headspace mixing however, it is stated that there is a lack of information specifically regarding headspace mixing of static closed chambers and that more information is needed to

improve the chamber design guidelines and to ensure consistency between researchers (de Kleine et al., 2012).

This experiment aims to investigate the effect of headspace mixing using fans on measured N₂O emissions from static closed chambers. N₂O emissions from chambers with and without fans will be measured to assess the relative difference in N₂O emissions. Vegetation may affect the flow of air within a chamber therefore this will also be taken into account through the comparison of emissions from chambers with and without vegetation. The effect of headspace mixing on two different sized static closed chambers (35 L volume and 112 L volume) will be assessed to determine whether the size of the headspace affects the need for headspace mixing. A preliminary experiment was also carried out in the field environment to assess whether a N₂O concentration gradient exists within a large static closed chamber.

Methodology

Preliminary experiment

Preliminary work was undertaken using a large static closed chamber in the field (70 cm height, 112 L volume). N₂O static closed chambers are commonly approximately 20 cm high, with a volume of around 35 L, however, to avoid damaging growing crops in the field, extensions are added which increase the chamber height. Due to the height of the extended chamber, the potential for an N₂O concentration gradient within the chamber could be an issue. Therefore, N₂O samples were taken from 3 heights (5 cm, 35 cm and 65 cm above the soil) within 8 large chambers in the field, each situated on a plot to which 200 kg N ha⁻¹ of synthetic NH₄NO₃ had been applied. Each chamber had an N₂O sampling port in the lid, from which a narrow piece of rubber tubing was inserted into the chamber, this could then be raised or lowered to different heights, allowing N₂O samples to be collected from the top of the chamber using a syringe.

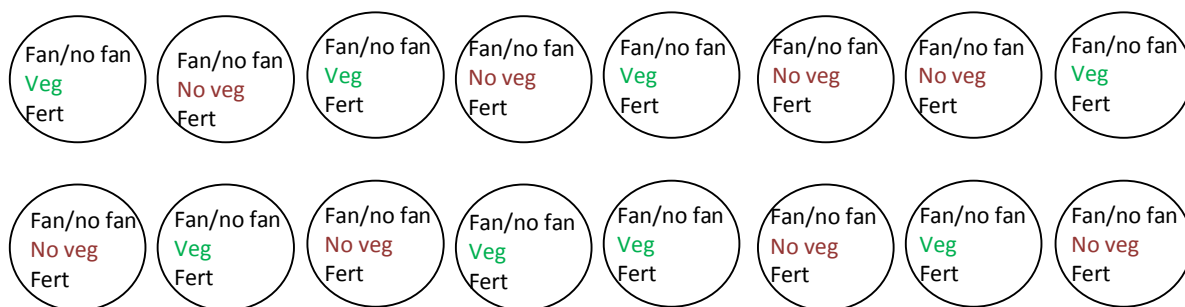
Site details of preliminary experiment, location of soil collection and main experiment

The preliminary experiment and the soil collection for the main experiment took place at Gilchriston farm, situated in East Lothian, Scotland as described in Chapters 4 and 5. The soil was collected from a field in which spring barley was growing and which had been fertilised with varying rates of NH₄NO₃ fertiliser as part of the experiment described in Chapter 5, however the soil was sampled from the field edges to try to avoid obtaining soil with widely ranging NH₄⁺ or NO₃⁻ contents. After collection the soil was thoroughly mixed to ensure homogenisation. The soil had a mean pH of 6.3, organic matter content of 4 % and a sandy loam texture. The main experiment took place in the SRUC glasshouse, beginning in March 2012. The natural temperature and daylight regime inside the glasshouse was considered suitable for plant growth at this time of year therefore the conditions were not adjusted.

Main experiment: Experimental design

Emissions from two sets of treatments were compared. The treatments were: Headspace mixing (fan) versus No headspace mixing (no fan) and Vegetation versus No vegetation. There were 16 replicates of each “fan” and “no fan” treatment, and 8 replicates of each “vegetation” and “no vegetation” treatment. In total there were 16 static closed chambers used in the experiment. The chambers were positioned randomly within a glasshouse compartment. Treatment names were as follows: Fan + no vegetation (fan + no veg), fan + vegetation (fan + veg), no fan + no vegetation (no fan + no veg), no fan + vegetation (no fan + veg).

Example experimental layout in the glasshouse: (randomly positioned chambers)



N₂O sampling, measurements and analysis

Approximately 12800 cm³ of soil was collected from Gilchriston, this was then divided between 16 trays (individual tray area of 160 cm²), so that each contained approximately 800 cm³ unsieved fresh soil. Trays of soil were placed on a bench in the SRUC glasshouse. Soil moisture content of each tray was adjusted to field capacity (60 % WFPS). Winter barley seeds of a mildew resistant variety were planted at a rate of 360 m² in 8 of the 16 trays. One (20 cm height, 35L volume) static chamber was placed on top of the soil in each tray, and inserted into the soil to a depth of approximately 5 cm, replicating conditions in the field. Each chamber had an aluminium lid which could be clipped onto the top of the chamber when N₂O measurements were taking place. One fan

was attached to the underside of each chamber lid, this aimed to reduce damage caused to the plants by moving fan parts compared to if fans were installed at the chamber base or sides. The fans had dimensions of 80 x 80 x 25 mm, voltage of 12V and a revolution speed of 3200 rpm. The fans were connected to 12V batteries and could be individually switched on and off as required, this allowed each chamber to act as both a mixed headspace and unmixed headspace treatment.

After the crop had been sown, N₂O emissions were sampled from each chamber to assess the background emissions of N₂O. To sample N₂O emissions, the aluminium lids were clipped to the top of the chambers and remained in place for 40 minutes. After this time, a sample of the headspace was taken through a sampling port in the lid and injected into pre-evacuated 20-22 ml glass vials. Six ambient gas samples from within the glasshouse compartment were also taken on each sampling occasion, as were four sets of samples taken every 10 minutes for an hour from four randomly selected chambers to check for the linearity of gas accumulation in the chamber (Chadwick et al., 2014). Measurements with fans/without fans were taken sequentially although the order in which measurements were taken (e.g. with fans 1st, without fans 2nd) varied. In order to ensure that there was no “carry over” of gas between measurements with/without fans, the chamber lids were removed and the chambers left open for 15 minutes before the next measurement was taken. By using all of the chambers for the fans/no fans treatments this ensured that all other conditions within the chambers were constant for the fans/no fans treatments (except diurnal effects although these should have been minimal as all measurements were taken within a time period of around 2 hours). On each sampling occasion the air temperature of the glasshouse was recorded for use in N₂O flux calculations.

Following the preliminary gas sampling, fertiliser (in the form of granules) was applied to all soil trays. The fertiliser was applied at a total rate of 200 kg ha⁻¹ N, 60 kg ha⁻¹ P

and 90 kg ha⁻¹ K. The fertiliser was split into 2 equal applications, the first application took place immediately following crop sowing, and the second application took place when the chamber extensions were added. Immediately after fertiliser application the soil was waterlogged to initiate an N₂O flux. For the first 2 weeks following fertiliser application, 4 gas measurements were taken per week, this decreased to twice per week until the next fertiliser application was received when the sampling frequency returned to 4 times a week for 2 weeks. This sampling frequency was chosen as it aimed to capture the high fluxes which usually occur soon after fertiliser application. Soil was watered regularly from above to keep the soil moist for plant growth with each tray receiving equal amounts of water. Once the plant had increased to the height of the short chambers, on day 21, the chambers were extended to a height of approximately 70cm to avoid damaging the growing plants. Extensions were also added to the short chambers on the no vegetation treatments to avoid confounding the results with different chamber heights. The experiment continued for 50 days, until the plants had reached their maximum height. The heights of each chamber above the soil (with and without extensions) were recorded.

Gas samples were analysed for N₂O concentrations using an Agilent 7890A Gas Chromatograph (GC) fitted with an electron capture detector (Agilent Technologies, Berkshire, UK) and a CTC Analytics COMBI PAL autosampler (CTC Analytics, Hampshire, UK). Linear regression was used to calculate daily N₂O fluxes and the trapezoidal rule was used to calculate cumulative N₂O fluxes by interpolating fluxes between sampling points.

Statistical analysis

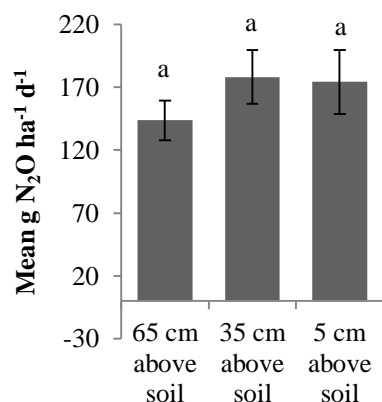
Statistical analysis of the data was carried out using Minitab software (16th edition). Differences between treatments were tested for significance using one way analysis of variance (ANOVA). Differences were assumed significant if $p < 0.05$.

Results and discussion

Preliminary experiment

The results of the preliminary experiment to test for a vertical concentration gradient within a large chamber in the field demonstrated that there was no significant difference between the N_2O concentration of gas samples taken at 5 cm, 35 cm and 65 cm above the soil (Figure 1). However, the lowest mean N_2O concentration of $144 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ was obtained at 65 cm height (i.e. the furthest away from the soil) as was hypothesised, and there was very little difference between the mean N_2O concentrations obtained at 35 cm and 5 cm height (178 and $174 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ respectively). Although there was no significant difference between N_2O concentrations at any height, there was an indication that a concentration gradient may exist with the lowest N_2O concentrations occurring furthest away from the soil. Another reason for the lack of a significant difference between the N_2O concentrations at different heights may be due to the small number of samples taken, only 8 samples in total were taken at each height, and this would likely have resulted in greater variability between samples than if a larger data set had been used. The results of the preliminary experiment combined with theory which proposes that a concentration gradient may exist within chambers suggested that the full experiment to investigate the effect of headspace mixing within chambers would be useful.

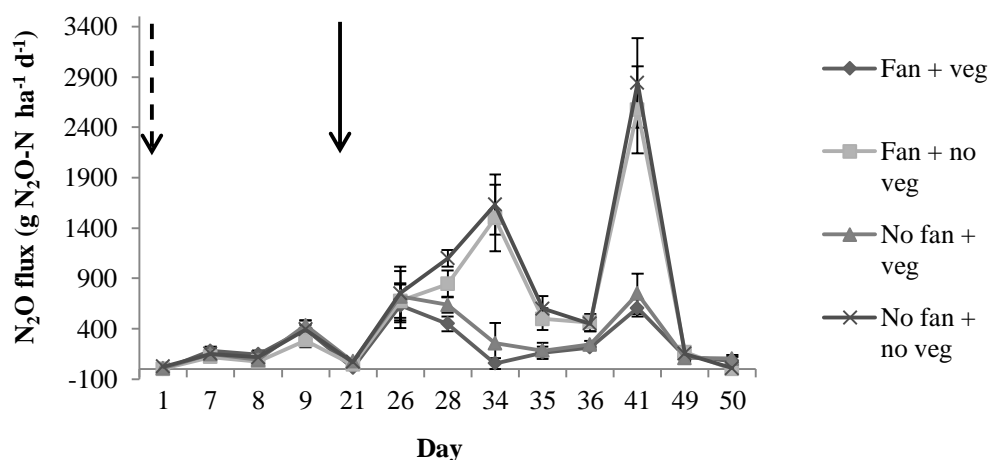
Figure 1). Preliminary experiment results: Mean daily N_2O flux from air samples taken at 5, 35, and 65 cm above the soil in eight 70 cm height chambers on 200 kg N ha^{-1} fertilised arable soil at Gilchriston farm. Different letters above bars indicate significant differences between treatments ($p < 0.05$).



Main experiment

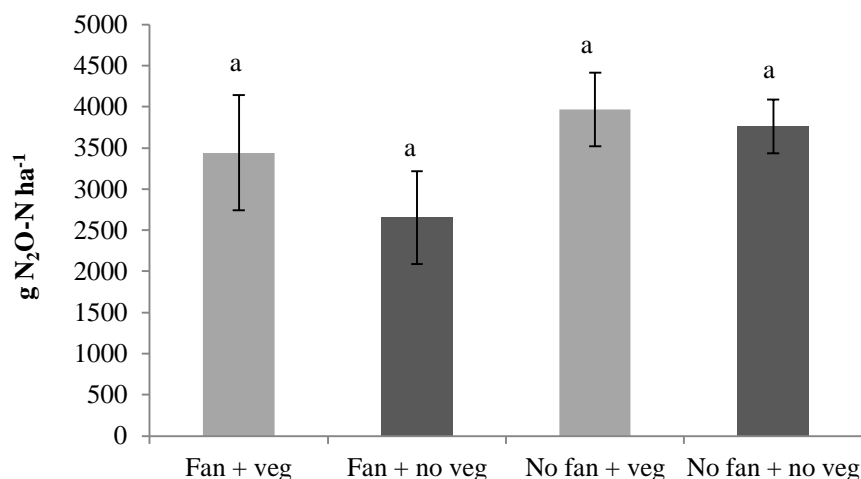
The daily N_2O flux from all of the chambers showed an increase following the first fertiliser application, and a larger increase following the second application (Figure 2). The maximum daily N_2O emission of $2841 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ was obtained from the “no fan + no veg” treatment. Prior to the second fertiliser application, emissions from all treatments were very similar, however, after the second application, emissions from the “no fan + no veg” and “fan + no veg” treatments increased and were greater than those from the “no fan + veg” and “fan + veg” treatments for the remainder of the experiment. This may be a reflection of the growth of the barley plants within the “no fan + veg” and “fan + veg” chambers, which by the time of the second fertiliser application were growing rapidly, and hence would have taken up the N applied in the second fertiliser application. This would have decreased the amount of N available for transformation into N_2O , resulting in lower N_2O emissions from the “no fan + veg” and “fan + veg” treatments.

Figure 2). Daily N_2O fluxes from all treatments over the 50 day experimental period. Dashed arrow indicates 1st fertiliser application, solid arrow indicates 2nd fertiliser application and addition of chamber extensions



Cumulative N₂O emissions from day 0-20, whilst using the short chambers showed no significant difference between any treatments, although emissions from the “fan + veg” and “fan + no veg” were lower than from the “no fan + veg” and “no fan + no veg” treatments by 13 % and 29 % respectively, possibly indicating an effect of headspace mixing (Figure 3). However, it must be concluded that whilst using short chambers (<20 cm) there is no benefit to measured N₂O emissions of using, or not using fans to mix the chamber headspace.

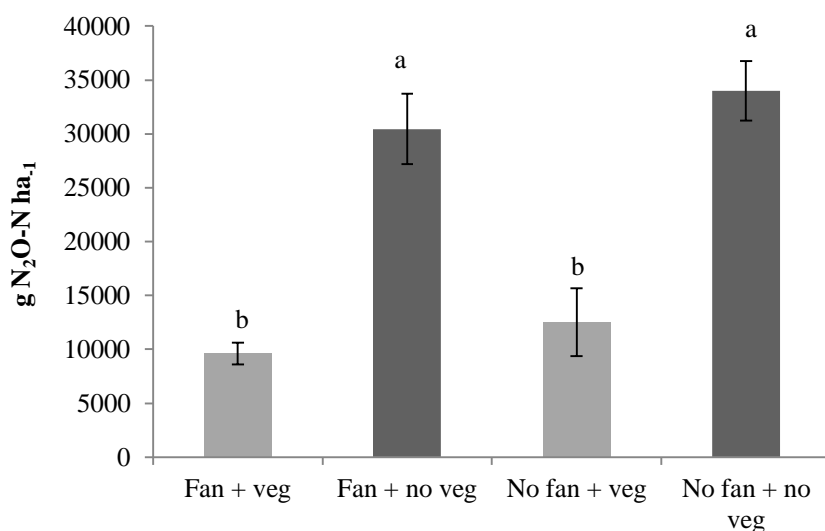
Figure 3). Cumulative N₂O fluxes from all treatments using short chambers from day 0 to day 20. Different letters above bars indicate significant differences between treatments ($p < 0.05$).



Cumulative N₂O emissions from day 21-50, whilst using the tall chambers, showed significantly greater emissions from the “fan + no veg” and “no fan + no veg” treatments than from the “fan + veg” and “no fan + veg” treatments (Figure 4). Again, this is a reflection of uptake of the fertiliser N by the growing barley plants in the “fan + veg” and “no fan + veg” treatments which decreased the availability of N for production of N₂O. Although there was no significant effect of headspace mixing on N₂O emissions, the emissions from the headspace mixed treatments (fan + veg and fan + no veg) were

lower than their respective non headspace mixed treatments (no fan + veg and no fan + no veg) by 23 % and 10 %, respectively. However, as with the short chambers, there appears to be no significant benefit to either using, or not using fans to mix the chamber headspace.

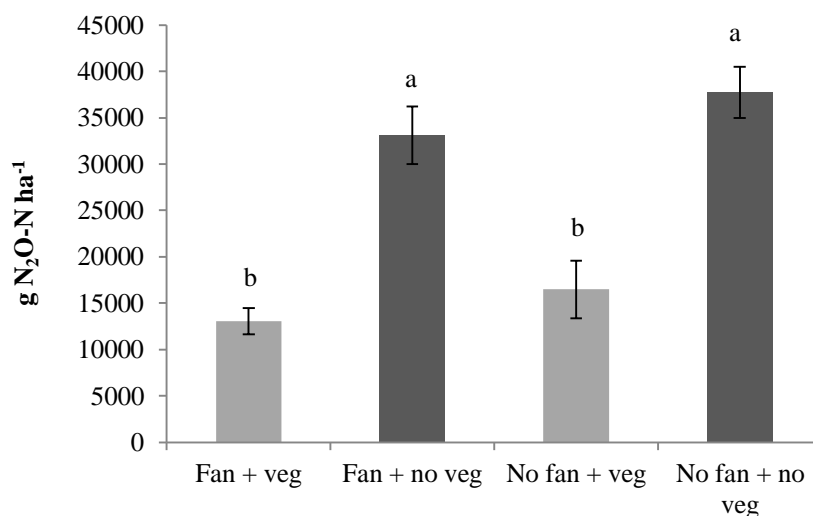
Figure 4). Cumulative N_2O fluxes from all treatments using short chambers from day 21 to day 50. Different letters above bars indicate significant differences between treatments ($p < 0.05$).



The differences between treatments as seen when using the tall chambers were also observed when cumulative emissions from the entire experimental period, (day 0-50) were analysed. The emissions from the “fan + veg” and “fan + no veg” treatments were 21 % and 12 % lower than from the “no fan + veg” and “no fan + no veg” treatments, respectively (Figure 5). Although there is no significant effect of headspace mixing on measured N_2O fluxes when using short chambers, tall chambers or a combination of both, there is a trend for lower emissions from the headspace mixed treatments in comparison to the non headspace mixed treatments, this is in contrast to the observed underestimation of fluxes obtained by Christiansen et al. (2011), when no headspace mixing was used. If a headspace concentration gradient does exist in chambers, and

samples are always taken from the top of the chamber then it would be expected that fluxes would be underestimated if headspace mixing did not take place. A suggested explanation for the lower fluxes observed in our experiment from the mixed rather than unmixed headspaces could be due to the positioning of the fan next to the sampling port on the chamber lids, in contrast to the positioning of fans at the base of the chamber by Christiansen et al. (2011). The fans hung slightly under the lids, leaving a gap of a few centimetres at the top of the chamber which may have been unmixed, and this is the location from which samples were taken. This indicates that if fans are used in chambers then the positioning in the chamber relative to the location of headspace sampling must be carefully considered, although potential damage to plants within the chamber must also be taken into account, which makes positioning of the fan anywhere other than on the underside of the lid very difficult.

Figure 5). Cumulative N_2O fluxes from all treatments for the entire 50 day measurement period. Different letters above bars indicate significant differences between treatments ($p < 0.05$).



Conclusion

The results of this study into the effect of headspace mixing on measured N₂O fluxes from static closed chambers indicates that for the chambers and fans used in this experiment, there is no observed benefit of using fans to mix the chamber headspace. There was a consistent (but not significant) decrease in measured N₂O fluxes when the chamber headspaces were mixed in comparison to unmixed, although further research into this would be necessary to determine whether this was an effect of headspace mixing, the fan positioning or possibly just random variation between the chambers. There was a significant effect of the inclusion of plants within the chambers on measured N₂O fluxes, with the inclusion of plants significantly decreasing N₂O fluxes, although this was independent of any headspace mixing effects. Although there is no significant effect on N₂O fluxes of either mixing, or not mixing the chamber headspace, it is recommended that fans are not included in chamber designs due to potential variations in the type of fans used which could confound results, and also the practical issues involving the installation and maintenance of fans (which would likely be more problematic in a field environment than in a glasshouse) and the potential for damage to plants within the chambers to occur.

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Appendix 3. Method development: Sterilisation of biochar by autoclaving

Introduction

Sterile biochar was required for use in the biochar batch sorption experiment (Chapter 7) to ensure that no microorganisms were present on the biochar as they may have influenced the results of the experiment. Autoclaving is commonly used to sterilise objects such as laboratory equipment, and as such was considered as a potential means by which to sterilise biochar.

Methodology

The biochars tested were the same as those used in the biochar batch sorption experiment (Chapter 7). Before sterilising the biochar, samples of biochar were placed onto PDA plates and Streptomycin was added to determine whether any fungi were present on the biochar. Subcultures of these fungi were grown and examined at 40X magnification under a microscope and the fungi present were identified. The autoclaving procedure involved subjecting the biochar to two cycles of autoclaving, each cycle lasting 30 minutes at 121°C. Following autoclaving, the biochar was once again placed on PDA plates with added Streptomycin to test for any growth of fungi.

Results

Before the biochar was autoclaved, fungi were present on the PDA plates containing UKBRC miscanthus, BTG miscanthus and mixed hardwood biochars. Following growth of subcultures of the fungi present and analysis under a microscope, it was suggested that the fungi present were as follows: UKBRC miscanthus: probably *Penicillium Polonicum*. BTG Miscanthus: *Paecilomyces variotii* and *Penicillium polonicum*. *Paecilomyces* can cause numerous infections in humans e.g. sinusitis, endocarditis. *Penicillium polonicum* can produce verrucosidin, a neurotoxin. Mixed hardwood: Include *Trichoderma*, *candida*. The images below (Figures 1-3) display the growth of

fungi on the UKBRC miscanthus, BTG miscanthus and mixed hardwood. Following autoclaving of the biochar there were no fungi present on the PDA plates.

Conclusion

Autoclaving of biochar was decided to be a suitable means of sterilising the biochar prior to use in the batch sorption experiment due to no growth of fungi on the PDA plates following autoclaving.

Acknowledgements

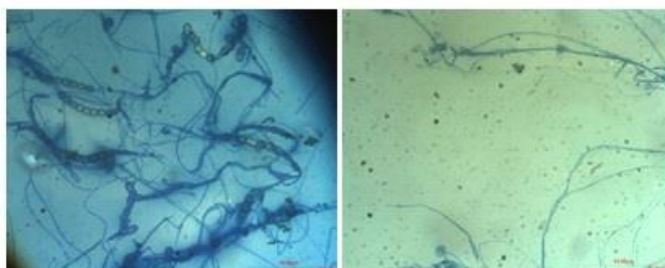
The help from Dr Oliver Knox in identifying fungi is gratefully acknowledged.

Figure 1. *Mixed hardwood biochar fungi growth before autoclaving*



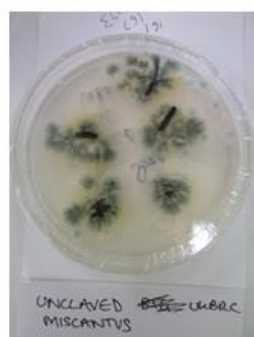
a). Original fungi growth

b). Subculture (viewed from front and back)



c) Subculture under 40x magnification

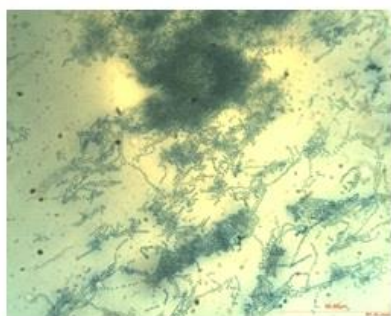
Figure 2. *UKBRC miscanthus biochar fungi growth before autoclaving*



a). Original fungi growth



b). Subculture



c) Subculture under 40x magnification

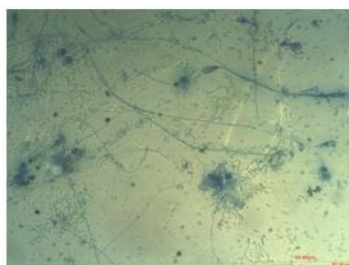
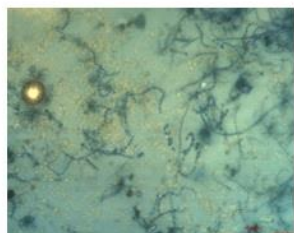
Figure 3. *BTG miscanthus biochar fungi growth before autoclaving*



a). Original fungi growth



b). Subculture



c) Subculture under 40x magnification